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THE PROBLEM OF PHYSICO-CHEMICAL PERIODICITY

FIG. 1.—The Periodic Crystallisation of Potassium Dichromate ($\times$ 25).

FIG. 2.—The Periodic Crystallisation of Benzoic Acid.

THE PROBLEM OF PHYSICO-CHEMICAL PERIODICITY

BY

E. S. HEDGES, M.Sc., Ph.D.

DEMONSTRATOR IN CHEMISTRY AT BEDFORD COLLEGE (UNIVERSITY OF LONDON), LATE DARBISHIRE RESEARCH FELLOW IN THE VICTORIA UNIVERSITY OF MANCHESTER

AND

J. E. MYERS, O.B.E., D.Sc., A.I.C.

SENIOR LECTURER IN CHEMISTRY IN THE VICTORIA UNIVERSITY OF MANCHESTER
LATE BEYER RESEARCH FELLOW IN SCIENCE

WITH A FOREWORD BY

PROFESSOR F. G. DONNAN

C.B.E., M.A., Ph.D., D.Sc., F.R.S.

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PREFACE

Although during the last hundred years reports of periodic physico-chemical phenomena have appeared from time to time, no attempt has been made to find a general principle covering the various manifestations in which this property is revealed. Indeed, most of the cases have been regarded as curiosities or anomalies and many have been forgotten entirely.

In the present work, in addition to presenting an account of the investigation of periodic chemical reactions which is in progress, we have attempted to classify periodic phenomena in general and to give a connected survey of the work in different fields, indicating wherever possible the interrelations of the results of different investigators. We are not in a position at present to offer a complete theory, but we have advanced a tentative hypothesis of a general nature.

The literary research has been rendered unusually difficult by the fact that in a large number of cases the reports of periodicity occur in papers relating to quite different subjects and are only mentioned as of passing interest. Nevertheless, we believe that the bibliography is very nearly complete up to the time of going to press. In order to preserve the uniqueness of the bibliography we have placed all the references to periodic phenomena together at the end of the book, whilst references not directly concerned with periodicity are placed as footnotes throughout the text.

We wish to record our indebtedness to Prof. F. G. Donnan, F.R.S., who has written a Foreword, to Dr. J. Holker and Mr. D. H. Bangham, M.A., for the communication of some unpublished work, to Miss Aileen M. Born, B.A., for assistance in checking the references and in the indexing, and to the Council of the Chemical Society and the Editor of the *Journal of Pathology and Bacteriology* for permission to reproduce certain of the illustrations.

E. S. H.
J. E. M.

July 8, 1926.

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Fig. 1. The Periodic Crystallization of Potassium Dichromate (× 25).

Fig. 2. The Periodic Crystallization of Benzoic Acid. *Frontispiece*

The Periodic Opacity of Wassermann Antigen with progressively increasing Concentrations of Sodium Chloride . *To face p.* 30

FOREWORD

By PROFESSOR F. G. DONNAN, C.B.E., F.R.S.

The subject of periodicity, rhythmic pulsation or intermittency in connexion with chemical change is one of very great interest and importance. This is also true of the periodic or regularly spaced " structures " which sometimes result from such actions, as for example the well-known Liesegang rings, or the various cases of a somewhat similar character which occur in certain natural objects, both inorganic and organic. Although these phenomena have already received a considerable amount of investigation the underlying causes are still very largely obscure.

In the present Monograph, Dr. Myers and Dr. Hedges have done an excellent service to science in giving a connected survey of the literature of research on these subjects, including an account of their own interesting investigations. It is a great advantage to have the whole material collected and examined in this way.

The authors have greatly contributed by their own discoveries to the elucidation of the phenomena of periodic and pulsating chemical action and have suggested a very interesting and general hypothesis.

Their Monograph is therefore much more than a critical summary of the existing scientific literature and constitutes a distinct and valuable advance in the theory of the subject.

The present work may be warmly commended to the attention of biologists and geologists as well as chemists and physicists.

F. G. DONNAN.

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CHAPTER I

INTRODUCTION

Chemical reactions proceed as a rule in a smooth, continuous manner according to quite definite laws which may be expressed in simple mathematical terms. A typical example is the continuously decreasing rate of evolution of hydrogen during the dissolution of a metal in an acid whose strength is being continuously diminished thereby.

It is proposed to show in the following pages, however, that in addition to this normal type of reaction, there exist many instances of *periodic reactions* or of periodic effects produced as a result of physico-chemical processes. This property is very widespread and is expressed in various ways. In general the word periodicity may be defined as the recurrence of some property or accentuation of a property at regular intervals of time, distance or other quantity. As a striking example of the periodic property we may refer in passing to the frontispiece, which shows the periodic crystallization of benzoic acid. Here we have a periodic structure recalling naturally occurring forms.

In this chapter it is proposed to review the general types of periodic processes and in the following ones to examine these types in detail. Before doing this it will be well, perhaps, to mention that many of the processes under review show a periodicity in which the "pulse," of whatever kind it may be, is observed in a positive direction only. Thus, in the periodic dissolution of metals, there are, at definite time intervals, sudden increases in the rate of evolution of hydrogen, but there are not corresponding decreases in the rate.

For this reason, the term "oscillation" is not immediately applicable to such cases, since this would imply a variation in the property in positive and negative senses alternately. The observed periodicity is not necessarily entirely dissociated from some process which is essentially oscillatory, for the periodic processes may be the observed results of fundamental oscillatory functions in which either "positive" or "negative" effects are suppressed or ineffective in regard to the property under observation. Something in the nature of a rectifier may convert an oscillatory property into one which appears finally as a pulsation.

It is necessary that a consideration of the problems arising out of periodic phenomena should be as wide as possible since there is already evidence that some of the various manifestations of periodicity are attributable to a common origin, and though we cannot at the moment offer a complete theory covering the various aspects of the phenomenon there seems to be little doubt that such a theory will be forthcoming in due course. We may now proceed to the preliminary survey of the field.

Static Periodicity.—There are a number of cases to which we propose to assign the description of "static periodicity," where the periodic property is expressed in terms of some quantity other than time or distance. In this type, a *periodic* change takes place in some property of the system under *continuous* change of some condition such as concentration, pressure, temperature, etc. A very striking example of this type is provided by the periodic opacity phenomenon of Holker, who has shown that the opacity of certain colloid systems varies periodically with continuously increasing change in the concentration of one of the components of the system. The type is also exemplified in certain phenomena associated with the hardening of metals.

It may be mentioned in connexion with static periodicities that the quantity which shows the periodic feature appears to be determined at once at any given point by the continuously varying factors and there does not appear to be any evidence that a given value of that quantity is arrived at by a periodic process. This state of affairs presents some difficulty, but it should be stated that work on this type has not as a rule been directed towards discovering evidence on this aspect of the matter.

Periodic Structures.—Another group of periodic phenomena which we have called "periodic structures" appears to be closely allied to the static periodicity just described. Examples of this group are to be met with in both natural and artificial systems, in which two reactants, very often in presence of a colloid or themselves producing a colloid, give rise in the course of their interaction to a periodic structure. Of these the Liesegang phenomenon is the best known and a very large amount of work has been done with a view to its interpretation. Here we have the interaction of silver nitrate and potassium dichromate in presence of gelatin giving rise to the formation of concentric rings of silver dichromate if the reaction is carried out on a plane surface, or producing parallel layers if a test tube is used.

The work on this subject has brought to light a number of other cases of a similar kind and an account will be given later of the various interpretations which have been placed on the

general phenomenon. Most of the work done on the subject has been concerned with the completed structures, but it would appear that these may be due to the operations of the same property which gives rise to the cases of static periodicity. Among the natural examples of periodic structures may be mentioned the agates, whose cross-sections recall very vividly the Liesegang rings, but in many cases such as urinary calculi and tree trunks it is difficult to rule out the possibility of external periodic changes as the real cause.

Another interesting group of periodic structures which have received little attention may be regarded as instances of periodic effects produced by the application of an apparently constant force. For example, the present authors have observed that if a tarnished cobalt rod is passed through steel rollers the metal emerges as a strip which is evenly marked by alternate bright and dark bands in a direction transverse to that of its movement through the rollers. The metal, having been rendered brittle by this treatment, may easily be broken in the fingers, the fractures occurring at the boundaries between the bands. Another similar case is that reported by Alkins in which the cold-drawing of copper wire apparently caused a periodic variation in susceptibility to corrosion, so that after exposure to the air, regular banding by alternate deep and mild corrosion was produced along the wire. The influence of external force such as is obtained by rolling or drawing or scraping appears to be very important in imparting periodic properties to metals.

Time Periodicities.—The next type which will be considered is that in which the velocity of a chemical reaction varies periodically with time. These time periodicities present a great interest both on their own account and also in reference to their possible relation to biological time periodicities such as the heart-beat. The observation of a periodic evolution of hydrogen from a dissolving metal is strongly reminiscent of such a process.

The best-known case is that originally reported by Ostwald, who found that the evolution of hydrogen accompanying the dissolution of chromium was most remarkably periodic. Ostwald devoted a great deal of attention to this case, but was eventually baffled by the fact that when the original batch of chromium was used up he was unable to reproduce the phenomenon. He employed all kinds of means to recover the periodicity, and the fact that beer and honey were among the things added to the reaction system to induce periodicity will indicate that little was left untried. Another case of a similar kind is shown by the periodic catalytic decomposition of hydrogen peroxide by various substances. On account of its relative simplicity this case is of

considerable importance, since it appears to offer special opportunities for throwing light on the general problem. It may also prove to be a connecting link between the phenomena of periodicity and those of catalysis.

It may be mentioned here that the relation between the static periodicities and the time periodicities may be concerned with a property of periodic adsorption, where the amount of substance adsorbed by a surface varies periodically with the concentration of the substance. Some evidence on this point has already been obtained.

Electrochemical Periodicity.—Another aspect of the periodicity exhibited by certain chemical reactions occurs in electrochemical phenomena, and although there is no difference fundamentally between these types it is convenient to treat them separately. Two possibilities are open in such phenomena and they have both been realized. Periodic phenomena may occur when current is being taken from a cell and also when it is being led through the cell. Examples of the latter case are treated according to whether they take place at the anode or at the cathode.

It has been established by the present authors that the periodic evolution of hydrogen in the case of the dissolution of metals in acids is concomitant with a periodic electropotential change. The experimental method of attack on the problem has therefore been improved and an explanation of the underlying cause has been advanced, as will be shown, by the demonstration of the fact that the seat of the periodicity in these cases is a metallic surface, and that the periodicity is associated with a certain metastable condition of that surface.

General Experimental Conditions.—It may be well now to make reference to certain conditions which appear to be essential in many cases if periodic phenomena are to take place, and which are important from both the experimental and theoretical standpoints. In the first place periodic phenomena, and particularly those associated with time, are very sensitive. It appears from the work of the present authors that the presence of extremely small quantities of various substances may induce periodicity, or may prevent it, or may act catalytically without producing a periodic process so far as can be determined. In several cases it has not been found possible to identify these substances. Again, it is not easy in some cases to demonstrate periodicities of high frequency owing to experimental difficulties, though there is no reason to doubt their existence, and if a given type of apparatus fails to reveal a periodic process it does not necessarily follow that no periodicity exists. On the other hand,

where the waves come to an abrupt end it is reasonable to suppose that the periodic property has ceased to act, though a reaction with a continuously increasing frequency which finally traces a straight line on a self-recording instrument is in all probability still periodic.

Failures to obtain Periodic Properties.—Another feature of work on periodic processes is the failure of what have been assumed to be the carefully determined conditions to bring about the necessary state of affairs. Ostwald's difficulties have already been mentioned. Antropoff sometimes found difficulty in realizing exactly the conditions necessary to ensure the periodic decomposition of hydrogen peroxide by mercury and discovered the method of cleaning the reaction tubes to be of importance. Reports of failure have been made by Köhlichen and by Küster and by others who have investigated cases of periodic electrolysis, and in these cases changes in the nature of surface of the electrodes appeared to be responsible. Kohlrausch made many unsuccessful attempts to repeat his periodic electrolysis of platinum tetrachloride and there are to be found in the literature other cases similar to Von Euler and Brandting's failure to repeat the periodic action of urease on urea described by Groll.

It has been shown by the present authors that one of the factors contributing to this state of uncertainty appears to be an ageing property which is frequently shown by colloids, and in the case of metals a similar result is produced in some cases by the transition of an active metastable surface into an inactive stable one. Such transitions may occupy a matter of minutes or hours or they may be going on for days or weeks.

Effects of "Poisons."—Another occasional source of difficulty is that small quantities of many catalytic poisons inhibit periodic activity. Formaldehyde, potassium cyanide and sodium arsenate are among the substances which have been recognized as poisons, and they have a progressive effect with increasing dosage. Small quantities diminish the frequency of the periods, and larger amounts stop it altogether. Chloroplatinic acid has been found to increase the rate of dissolution of metals in acids enormously, but to inhibit periodicity, as far as can be observed.

In the succeeding pages it is proposed to discuss in some detail the work on various types of periodicity. This survey will probably suggest that there are grounds for thinking that some fundamental principle exists which is responsible for the various manifestations of periodicity, and it is the opinion of the authors that this property is associated with surfaces and is probably a function of surface energy.

One or two general matters may be mentioned before proceeding to this detailed discussion. If certain assumptions are made as to the mechanism of series of consecutive reactions, it can be shown mathematically that the rate of formation of the final product will be periodic. At present none of the known cases of periodic chemical reactions can be reconciled with the mathematical requirements: further, the equations denote a true oscillatory change in place of the pulsation which is found in practice. In an article entitled "Rhythm in Nature" Flatelly discusses many types of periodic phenomena, chiefly biological and meteorological, and concludes that rhythm is an indicator of efficiency. Several examples are quoted where functional disorders are betrayed by irregularities in some rhythm. As a practical application of such a principle may be mentioned accelerated filtration by increasing the air pressure in pulses. It has been suggested elsewhere that the efficiency of the kidney in excreting urine is increased by the pulsating course of the blood.

Possible Biological Significance of Periodic Action.— In addition to the importance of the problem of periodicity from the physico-chemical standpoint, several investigators have been struck by the suggestive similarity between physical cases of periodicity and the periodic processes and functions of living organisms. On this point the authors would indicate that there are various features of physical periodicity which lend colour to this idea. The physical cases are very often associated with metastable surfaces: they are often very sensitive and operate between narrow limiting conditions: they are of a pulsating rather than an oscillatory character, and the time periodicities show frequencies of great variety. It may therefore be that the biological periodicities have their origin in a physical property, though at present this can only be regarded as speculative.

CHAPTER II

STATIC PERIODICITY

The classical example of this type is the rule enunciated by Lothar Meyer and by Mendeléeff, that the physical and chemical properties of the elements vary periodically with increasing atomic weight. Numerous experimenters have since compiled data which testify to the wide ground covered by this generalization. The literature on this subject is already prodigious and it is not intended, therefore, to make further reference in the present work. It may be pointed out, however, that the principle of periodicity concerns the very fundamentals of chemistry. From time to time, reports have appeared of periodically changing properties of substances under continuous change of external conditions. An example of such is the observation of Tingle and Rolker concerning the melting-points of mixtures of ortho- and para-nitranilines. A periodic curve is obtained when the melting-points of the mixtures are plotted against percentage composition.

Several cases of periodic changes taking place during the cold-working of metals are on record, and these are of particular interest in connection with experiments on the periodic dissolution of metals described in Chapter IV. Thus, Young and Van Sicklen, in some hardness tests of steel, found the hardness to vary periodically with the number of impacts received. Again, Portevin and Le Chatelier observed that, during the process of hardening of certain magnesium-aluminium alloys, the tensile strength varies periodically with the load. Le Chatelier observed a similar effect in certain steels. Both Ellis and Johnson give curves showing that the progressive cold-rolling of copper is accompanied by periodic changes in tensile strength, lateral spread, elongation, Brinell hardness and scleroscope hardness. Smith and Turner have studied the effect of progressive cold-rolling on sterling silver and on a silver-copper-cadmium alloy, and the hardness of the product is in both cases periodic with respect to the amount of work done on the metal. According to Alkins, the susceptibility to corrosion of hard-drawn copper wire varies periodically along the length of the wire, and this he ascribes to a periodic difference of electropotential along the wire. Reference may also be made to the work of Borelius and Gunneson, who have observed that the emission of occluded nitrogen

or hydrogen from iron varies periodically with a steadily rising temperature, and that the thermoelectric properties of iron vary in a similar way.

Another example of static periodicity where temperature is the continuous variable is the observation of Huntington that the tensile strength of copper and of certain copper alloys is a periodic function of the temperature of testing. The amplitude of the effect was decreased by previously annealing the copper.

An interesting example of the static type of periodicity associated with metals is the observation by Palmer and Constable that the catalytic activity of copper, prepared by reduction from the oxide, varies periodically with the temperature of reduction. Constable considers that the orientation of planes at the surface of crystal grains changes with rise of temperature. Since some planes are more active than others, a periodic variation will be noticed.

Mention of Spring's observation, that there are periodic concentration optima in the protective action of soap on ferric hydroxide, leads to a consideration of the most important recent addition to this branch of the subject—the work of Holker [2, 3, 4] on the opacity of precipitated colloids. The method of experimentation employed by Holker * was to take a series of Jena glass tubes containing the colloid solution and add to each successive tube an increasing quantity of an electrolyte in solution. The degree of turbidity of the contents of each tube was determined after leaving at 40° C. for four hours with shaking every hour. The colloids studied were various animal sera, gelatin, gum acacia, agar, gum mastic and dialysed hæmoglobin. The electrolytes used were sodium chloride, potassium chloride, calcium chloride, hydrochloric acid and caustic soda.

In Fig. 1 the curves represent the opacity of human serum diluted five times with progressively increasing concentrations of sodium chloride. The marked periodicity is typical of most of the systems which have been examined. Further experiments with human serum indicated that, with rise of temperature, the amplitude of the waves increased, the wave-length remaining constant. Both the amplitude and frequency increased for stronger solutions of serum. The periodicity was no longer observable when the serum was diluted to 1 part in 400.

It does not appear that a colloid need be present initially, for periodic opacity curves were obtained in the precipitation of a " buffer " sodium phosphate solution by progressively increasing concentrations of calcium chloride. Precipitation of disodium

* The opacimeter used by Holker is described in the *Biochemical Journal*, 1921, **15**, 216.

hydrogen phosphate or sodium dihydrogen phosphate alone with calcium chloride did not give a periodic curve. It is interesting that the best effect was obtained when the two salts were present in the ratio in which they exist normally in blood. It should be mentioned that, although in such a case as this there is no colloid present initially, the precipitate itself is of colloidal dimensions: in fact, Holker has repeatedly noticed that periodicity is not to be

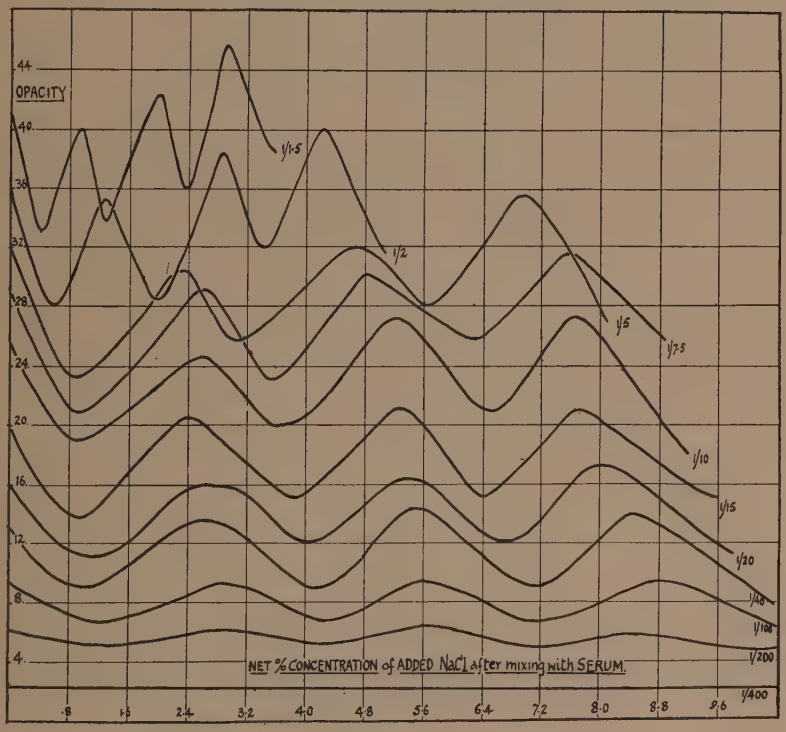

FIG. 1.

The opacity of Human Serum diluted with progressively increasing concentrations of sodium chloride. (After Holker.)

observed under conditions such that the precipitate is about to settle.

In the instances which have been mentioned, the change is observed by means of the opacimeter constructed by Holker. There are, however, cases where the periodic change in turbidity is obvious to the unaided eye. Such an effect is exhibited by Wassermann "antigen" when sodium chloride is the added electrolyte (Holker [3]). Plate II, Figs. 1–7 (p. 30), is a photograph

of a series of test-tubes containing Wassermann antigen diluted to 1 in 85, to which were added progressively increasing concentrations of sodium chloride from 0 to 32 per cent., each successive tube being 0·5 per cent. stronger in sodium chloride than the preceding one. In this case there are two complete periods.

This system is extremely complicated, but theoretical consideration has been made easier to some extent by the observation that a visibly periodic precipitation occurs when successive tubes containing water-glass are treated with progressively increasing concentrations of hydrochloric acid.

CHAPTER III

PERIODIC STRUCTURES

Historical.—During the course of staining histological specimens by Golgi's method, an interesting phenomenon, which has proved to be productive of a large amount of research, was observed by Liesegang [1] in 1896. If a drop of fairly strong silver nitrate solution be placed on a sheet of gelatin impregnated with a small quantity of potassium dichromate, reaction between the electrolytes takes place in the gelatinous medium with precipitation of silver dichromate. Under these conditions, however, the precipitate is not continuous, but forms a series of concentric rings separated by clear spaces in the gel.

Such rhythmic formations are customarily called "Liesegang's rings," and, in fact, it is to Liesegang [2, 3, 4, 5] that we owe the first systematic study of the phenomenon. Hepburn has pointed out, however, that this periodic precipitation was known to Lupton as early as 1892, and the rhythmic banding of calcium oxalate was described by Ord in a book entitled *The Influence of Colloids on Crystalline Form and Cohesion*, published in London in 1879. The first discovery of the phenomenon is traced by some to a book appearing in 1855, printed by the author, G. Runge, and entitled *Der Bildungstrieb der Stoffe*. This consisted of a series of sheets of porous paper soaked with aqueous solutions of metallic salts which reacted with each other at the boundaries. Runge's main thesis was the life-like form of the resultant substances produced under these conditions.

Methods of Experimentation.—Liesegang himself was quick to realize the importance of the phenomenon in the explanation of laminated biological [17, 20] and geological [10, 13, 18] structures, and suggested that agate-like formations were caused by the diffusion of metallic salts into a mass which was formerly gelatinous silicic acid. The periodic formation is by no means restricted to silver dichromate, nor need gelatin be the reaction medium. Most subsequent experimenters have employed a somewhat different method from the routine at first followed by Liesegang. The gel, containing a small quantity of one of the reacting salts, is allowed to set in the lower part of a test-tube and a stronger aqueous solution of the other reactant is subsequently poured on top. Slow diffusion of the stronger solution

into the gel takes place, with the production, in this case, of a series of bands or discs of precipitate corresponding with a thin strip cut out of a ring formation. By using a U-tube in place of the test-tube the effect of two different diffusing agents can be studied simultaneously.

Hausmann carried out a large number of experiments in various gels, obtaining rhythmic banding of many different substances. He further observed that, in the original case of periodic precipitation of silver dichromate in gelatin, the intervening spaces separating the rings of precipitate gradually developed a series of secondary rings packed very closely together. Schleussner [1, 2] has recently shown that these intermediate rings, which are to be observed with the aid of a lens, are due to chlorides and phosphates originally present in the gelatin, and suggests that the character of ring formation is an index to the purity of the gelatin. Descriptions of other cases are given by Stansfield and it would appear that, given suitable conditions of concentration and other factors, rhythmic banding can be realized with any pair of interacting salts. Rayleigh [2] describes the periodic precipitation of silver arsenate in gelatin, and Hatschek [3] obtained bands of copper phosphate in a silica gel, whilst many others have obtained rhythmic structures of various insoluble salts in agar gels.

A few of these examples warrant attention in virtue of their novelty. Holmes obtained bands of cuprous oxide by diffusing copper sulphate solution into a silica gel containing glucose. By allowing oxalic acid to diffuse into 1 per cent. gold chloride contained in a gel of silica, bands of colloidal gold separated by scattered golden crystals were obtained. Similar results had been realized earlier by Hatschek and Simon [1, 2] by reducing a gold salt in a silica gel by means of gaseous sulphur dioxide. These authors relate the phenomenon to the bands of colloidal gold sometimes found naturally in quartz. Rhythmic bands of Purple of Cassius were obtained by Davies.[4] Liesegang [16] has produced bands of silver in gelatin containing 2 per cent. ferrous sulphate by diffusing in 20 per cent. silver nitrate. Bechhold [2] produced rings by diffusing metaphosphoric acid into serum contained in gelatin, and Handowsky and Reymond succeeded in forming a series of stratifications of precipitate by diffusing some alkaloid hydrochlorides into a mixture of iodine and potassium iodide contained in a gelatin gel.

Others have obtained similar effects under somewhat modified conditions. Creighton passed a current between iron electrodes through an agar gel holding in solution a mixture of potassium ferricyanide and sodium chloride and obtained bands of Turn-

bull's Blue. Using a mixture of sodium chloride and phenolphthalein, alternating discs of green ferrous hydroxide and the red coloration of phenolphthalein resulted. Novel methods of experimentation are also described by Janek [1, 2]. Möller has prepared laminated structures by diffusing silver nitrate into wheat grains and the leaves of some plants, and a similar effect was produced by Seidel in root-fibres of wheat, oats and rice. A periodic plasmolysis was effected by allowing glycerol to diffuse into such a fibre kept in a film of water. Macallum and Menten have produced such structures in nerve fibres.

Theories of the Liesegang Phenomenon.—The first attempt at an explanation of this phenomenon, which has since been found of such general occurrence, was put forward by Ostwald [1] in 1898. He supposed that the silver nitrate and potassium dichromate diffused into each other, forming a supersaturated solution of silver dichromate which did not immediately precipitate. By the time the precipitate had formed at the boundary of the reacting substances, the gel in the immediate vicinity of the precipitate had become impoverished of potassium dichromate, so the advancing silver nitrate had to travel some distance before it could again make the supersolubility product with the dichromate ions. This accounts for the spaces in between the bands of precipitate. That the potassium dichromate does move towards the silver nitrate has been demonstrated by Licsegang.[8] A tube containing potassium dichromate in a gelatin gel is placed in a silver nitrate solution, which diffuses in at both ends. Band formation commences from both extremities and finally a dead space free from dichromate remains in the middle of the tube. This result has been given other interpretations. Quantitative experiments by Morse and Pierce [1, 2] indicated that, before the precipitation of a band, the concentration of silver chromate was indeed greatly in excess of that required for saturation, and this has been taken as strong confirmatory evidence in favour of Ostwald's view. The deductions of Morse and Pierce have, however, been adversely criticized recently by Jablczynski.[1]

As early as 1905, Nell concluded that his experimental observations could not be reconciled with the views of Ostwald. Shortly afterwards, Liesegang [7] performed an experiment which he considered completely refuted the supersaturation view. After a series of rings had been formed in gelatin on a glass plate by the diffusion of a drop of strong silver nitrate into dilute potassium dichromate, a quantity of potassium dichromate was then placed on the spot originally occupied by the silver nitrate. This, in its turn, diffused and reacted with the excess of silver nitrate, form-

ing a second series of concentric rings, which were quite independent of the first series. Some years later, Liesegang [9] noticed that the second series of rings produced by this method occurred at a different level in the gelatin layer, and thenceforth he became an ardent supporter of Ostwald's explanation. Hatschek [4] countered this by obtaining bands of lead iodide by diffusing lead nitrate into an agar gel containing potassium iodide and sown with crystalline lead iodide. There was no possibility of supersaturation under such conditions, according to Hatschek. Dhar and Chatterji [2] object that the ordinary relations may be modified in a gel, for colloidal silver chromate in gelatin was not coagulated by crystalline silver chromate even after several days. Hatschek [5] has also pointed out that if the experiment designed by Liesegang to deny his own first impression be carried out in a tube instead of on a plate, the same result is obtained although there is no chance of the two series of stratifications being at different levels. Examples which cannot be explained on a basis of supersaturation are given by Füchtbauer, who obtained bands of chloroform by diffusing caustic potash into an agar gel containing chloral hydrate, and by Davies,[1] who effected a rhythmic precipitation of mercury in agar containing sodium formate, by diffusing mercurous nitrate into the gel. Supersaturation effects in the ordinary sense are ruled out here. An experiment made by Bechhold [2] seems to be quite beyond the range of Ostwald's theory. Gelatin containing globulin and sodium chloride was placed in a test-tube and covered with a layer of water. As the sodium chloride diffused *out*, the globulin precipitated out in the form of banded turbidities.

A factor which had been formerly overlooked was suggested by Bechhold.[1] This was the solubility of the precipitate in the reaction medium. He showed that in the rhythmic precipitation of silver dichromate by the interdiffusion of silver nitrate and ammonium dichromate, the silver dichromate is somewhat soluble in the ammonium dichromate and also in the ammonium nitrate produced. He suggested that the ammonium nitrate produced in the first precipitation zone prevented precipitation of more silver dichromate in the neighbourhood. This does not seem to have a very wide application. Bechhold [2] also obtained precipitation in zones between two colloids by diffusing goat serum into gelatin containing the serum of a rabbit which had previously been inoculated with goat serum. From other experiments Bechhold * finds that in many cases colloids mutually precipitate each other only when in definite ratios and solution takes place in presence of excess of either constituent. These experiments

* *Z. physikal. Chem.*, 1904, **48**, 418.

are supported and confirmed by Buxton and Shaffer.* It is therefore suggested that this property of colloids plays a part in ring formation.

It is generally accepted that the precipitated substance in these reactions is first formed in a colloidal state, but, according to Williams and Mackenzie, silver chromate exists in gelatin as a crystalloid. Alexander, however, points out that at the dilutions used the precipitated silver chromate would be so finely dispersed as to show a measurable diffusion, although colloidal. Quite recently, Sen and Dhar have come to exactly the opposite conclusion to that arrived at by Williams and Mackenzie. Fischer and McLaughlin believe that the formation of a colloidal, semipermeable membrane of precipitate is a necessary prelude to band formation. The membrane slowly crystallizes and lets through some of the diffusing solution, which then forms a new semipermeable membrane. Other attempts at explanation, founded on the colloidal nature of the precipitate, have been made by Freundlich and Schucht, who find the spontaneous precipitation velocity of colloids to be autocatalytic in character, and by Jablczynski and Klein, who consider the phenomenon to be due to the growth of large grains at the expense of the smaller as a result of diffusion. Similar suggestions have been made by Sekera. The supposed colloidal nature of the bands has been called into question by Hatschek.[10,1]

The question of grain size is certainly of very great importance in this matter. Although, in the original case discovered by Liesegang, the rings of silver dichromate are separated by quite clear spaces, a large number of those who have investigated the phenomenon using different substances have observed that, in the majority of cases, the rings contain a large number of small particles and the intervening spaces contain a small number of large particles. Hatschek [6] quotes the case of cadmium sulphide precipitated in silicic acid gel. Here, the precipitate consists of alternate pink and yellow bands, and, as is well known, the difference between the two forms is in the size of the particles. Hatschek [6] writes: "It is an open question whether, in many cases, the actual amount of reaction product in equal volumes of ring and clear space is not approximately the same." Dhar and Chatterji [2] also distinguish two kinds of ring formation: in one class a layer of precipitate is followed by a clear zone and, in the other class, a coagulated sol, which may in course of time crystallize, is followed by a zone of peptized sol.

By far the best known of the theories which take into account the colloidal nature of the product is that of Bradford.[1, 2, 3]

* *Ibid.*, 1906, **57**, 47.

According to this view, the spaces in between the rings are to be attributed to the adsorbent effect of the precipitate on the electrolyte in the immediate vicinity. Thus, in the ordinary Liesegang phenomenon, the silver chromate adsorbs some of the potassium chromate in the gel, leaving a clear space through which the silver nitrate has to travel before it meets any more chromate. It is said that this clear space can be seen when a coloured substance is used. Band formation generally ceases before the bottom of a tube is reached (compare Liesegang's "dead-space" experiment) and this Bradford [4] cites as additional evidence in favour of adsorption of the solute by the precipitate. He [5] also points out that only precipitates possessing a large specific surface are given to band formation, and rhythmic structures may often be obtained or not at will by varying the specific surface and consequently the adsorptive capacity. Thus, by increasing the dispersity of silver chromate or silver dichromate, bands of both may be formed in agar —a result which had not been formerly achieved.

It is likely that such an adsorption does in some cases modify the effect, though it is probably a secondary influence. Bradford has never actually demonstrated that adsorption of this kind does take place to the extent required. On the contrary, Dhar and Chatterji [2] find that silver chromate is capable of adsorbing only a very small quantity of potassium chromate. These latter authors [1, 3] relate the phenomenon to the periodic peptizing influence of the gel on the colloidal reaction product. They [4] show that the coagulation of silver chromate sol is brought about by potassium chromate within certain concentration limits, outside which a yellow sol is produced. This seems to be a promising line of attack and recalls the periodic peptizing influence of soap observed by Spring (see p. 18) and the experiments of Holker (p. 18). Takehara has recently made a suggestion in this direction, pointing out the resemblance between the formation of Liesegang rings in gelatin gels and the formation of precipitates in gelatin sols at slightly higher temperatures. Precipitates are only formed when critical salt concentrations are exceeded.

Hatschek [11] has recently shown quite definitely that complete exhaustion of the reacting component in the gel under the last ring is not a necessary condition for the formation of another ring. This is in disagreement with Bradford's theory and with those theories which postulate a membrane formation, e.g. the theories of Fischer and McLaughlin, and of Traube and Takehara.

In the writers' opinion, the solution to the problem of this

type of periodicity is closely connected with the phenomenon discovered by Holker.[3] According to Holker the opacity of a precipitated colloid is in many cases a periodic function of the concentration of the precipitating electrolyte. Now, in the ordinary Liesegang phenomenon the concentration of the silver nitrate in the advancing wave of diffusion is subject to a progressive dilution, and consequently, according to this view, opacity bands are produced which correspond with the peaks of Holker's curves. The opacity of a suspension increases up to a limit with decrease in size and particles, and this explains very well the difference in size of particles between the bands and spaces mentioned by Hatschek. This, then, may be regarded as the primary cause of the periodicity, and it is no doubt modified by subsequent events such as adsorption, diffusion, growth of the larger particles, etc.

In fact, Holker (private communication) has analysed the Liesegang phenomenon by treating dichromate-gelatin solutions in successive test-tubes with progressively increasing concentrations of silver nitrate solution. The gel obtained on setting was a clear yellow in tubes containing less than 0·1300 per cent. silver nitrate. The maximum concentration used was 0·1390 per cent. and between these limits there were eighteen intermediate tubes. A turbid yellow was produced in the first two tubes, a turbid red in the next four, a turbid yellow in the next one, a turbid red in the next three, a turbid yellow in the next one, and a turbid red in the following five tubes. Thus, the periodic structure is closely allied to the periodic opacity phenomenon.

Periodic Structures in Absence of Chemical Reaction.—Such a view would suggest that rhythmic banding should take place, without any chemical reaction, simply by diffusing a solution into a colloid under a concentration gradient. Such results have been realized, but, unfortunately, in the majority of cases the turbidities are too faint to be perceived without the aid of some form of nephelometer : in fact, it may be said that the second substance, with which the diffusing agent reacts to form an insoluble salt, acts as an indicator. For example, Moeller [2] has produced bands of this type by diffusing silver nitrate solution into pure gelatin, and in the diffusion of hydrochloric acid into gelatin containing sodium chloride. Strata were also produced when gelatin gels were subjected to the action of tanning solutions. Moeller states that bands may be formed when any ionizable substance diffuses into a gel. Some other examples of this have been observed by Copisarow (unpublished). Stuckert has described bands at the boundary of the gel and sol

produced when sodium glycocollate or some other substances are placed on a gelatin gel.

Similar results have been effected by producing a concentration gradient by progressive drying of a gel containing a salt in solution. Liesegang [3] showed that a strip of 10 per cent. gelatin, containing 10 per cent. potassium dichromate, so arranged that drying progressed slowly from one end to the other, crystallized out in bands. Lüppo-Cramer describes rings formed on a photographic plate which was immersed in potassium oxalate solution and then allowed to dry. Rhythmic crystallization of trisodium phosphate, copper sulphate and some other inorganic salts was observed by Küster [4, 5] from gelatin solutions of these substances. Rohonyi reports that ice crystallizes out of thin films of gelatin solution, on freezing, in the form of concentric rings.

Some, notably Fricke, and Traube and Takehara, consider that the phenomena are explicable by the ordinary processes of diffusion as modified by the presence of the precipitate, without invoking the aid of any other factors. Wo. Ostwald has recently made the suggestion that the periodic structure is due to the interference of waves of diffusion set up by the diffusing electrolyte, the electrolyte contained in the gel and the products of reaction. Hatschek,[2] also, showed mathematically the possibility of formation of alternate layers by diffusion of particles of different mass. The banding of solutions, through which there was a temperature gradient, has been described by Liesegang.[19] Such bands can be fixed by using gelatin solutions and freezing quickly. A curious layer formation assumed by clay suspensions, in presence or in absence of electrolytes, when left undisturbed, has been observed by Ungerer. Williams also noticed stratifications in soil suspensions when these were exposed to diffused daylight. Morison has observed that the passage of a beam of light through suspensions of soil or kaolin contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between successive strata varies with the wave-length of the light, and the effect disappears slowly after removal of the source of the light.

McGuigan and Brough believe that periodic precipitation is the normal course and that, in the absence of a gel, the reaction is normally so turbulent as to mask the effect. They remark, prophetically, "There is some evidence that all chemical action may be periodic."

Effect of Conditions.

(*a*) **Concentration.**—In general, in any one system, the ring formation is dependent on the concentration of both reactants

and of the gel. Within limits, the distance between the bands decreases with increasing concentration of reactants and gel. Measurements of this sort have been made by Bradford [3] and by Stansfield. The latter concludes that ring formation is favoured by employing a strong diffusing agent and a dilute reactant. If the concentrations of the two are equal, a precipitate forms, which appears at first sight continuous, but which is seen under the microscope to be very finely banded. Köhler [2] states that the bands are only partly developed when the solutions are too weak and are blurred when too concentrated solutions are employed. In almost every case, the distance between successive bands increases, and Schleussner [2] has found this increase to conform with a geometric series. In the rhythmic precipitation of mercury effected by Davies,[1] however, the distance between successive bands was found to decrease. Popp recommends the rhythmic banding of magnesium hydroxide, produced by diffusing ammonia solution into gelatin gels containing magnesium chloride for quantitative investigation, since the bands are exceedingly sharp. The width of the strata and their distance apart were found to increase with decreasing temperature.

(*b*) **Light.**—Of recent years, considerable interest has been attached to the effect of light on rhythmic formation. Küster [3] conducted some experiments in which the tubes were periodically illuminated. Bands of silver dichromate and of silver chloride were formed, although, he states, no bands were formed in the dark. Davies,[2] however, obtained good bands in the dark. According to Dhar and Chatterji,[2] in silicic acid gels, band formation of lead halides is not affected by light, but in the case of silver chloride and silver iodide rhythmic precipitation took place in the light but not in the dark. It may be observed that Ganguly and Dhar * have found that light coagulates a silver chloride sol. Light also had an effect on the stratified precipitation of mercuric iodide. Odén and Köhler observed that light of short wave-length was most effective and a similar report has been made by Blair. Davies [2, 4] could not obtain bands of colloidal gold in silicic acid after Holmes's method, experimenting in the dark, and suggested that Holmes's results were due to experimentation in a changing light. Bands were obtained by covering tubes with black paper through which slits were cut at intervals. Hatschek [9] prepared stratifications of lead chromate and dichromate in agar and observed, in many cases, wide spaces between sets of bands. These were not developed in the dark, where the normal layers still appeared, and were

* *Kolloid Z.*, 1922, **31**, 17.

observed to form diurnally. The ordinary and anomalous bands could be made side by side in the same gel by screening one side and illuminating the other. Such secondary bands have been observed by Tryhorn and Blacktin with silver dichromate and with mercuric iodide. According to Tryhorn and Blacktin, these substances crystallize from gelatin solutions more readily in the light than in the dark. Liesegang [21] has suggested that the effects ascribed to light by Hatschek may be due to temperature differences. On the whole, although the effects ascribed to light are somewhat contradictory in places, it appears that it may exert a modifying influence in certain cases.

(*c*) **The Function of the Gel.**—Bancroft [1] objected (1921) that the attempts which had been made until then at explaining the phenomenon of rhythmic precipitation were deficient in that they failed to take into account the specific influence of the gel. It therefore becomes interesting to determine the extent of the rôle played by the gel. The apparent specificity of the gel is in many cases due to neglect of the alteration of conditions such as concentration, and many conflicting statements have crept into the literature on this account. McGuigan states that, reversing the usual Liesegang phenomenon, rings could not be formed by diffusing the potassium dichromate into the silver nitrate. This is refuted by Bradford.[6] Hatschek [6] states that silver dichromate readily forms bands in gelatin but not in agar, whilst lead chromate gives bands in agar and not in gelatin, and neither does in silicic acid. Others have found that, by suitably modifying the conditions, rhythmic banding may be obtained in these instances. Holmes has shown that at least in some cases the course of events is determined by the other substances present in the gel. For instance, in using silicic acid gels made from sodium silicate, the precipitating acid is of importance. He finds it best to use acetic acid. In preparing bands of mercuric iodide in silicic acid, the addition of fairly large quantities of sodium chloride completely inhibited the production of stratifications, and this explains the inability of experimenters who prepared their gel from sodium silicate by addition of hydrochloric acid to produce such bands.

The statement has been made that the gel is of fundamental importance in rhythmic precipitation. Zacharias has expressed this view. At one period, Liesegang [14] suggested that since rhythmic structures were in some cases dependent on "external rhythms" such as the diurnal variations of light intensity, they might also be dependent on "internal rhythms" taking place in the gel. According to Moeller,* gelatin gels contain two

* *Kolloid Z.*, 1916, **19**, 205, 231.

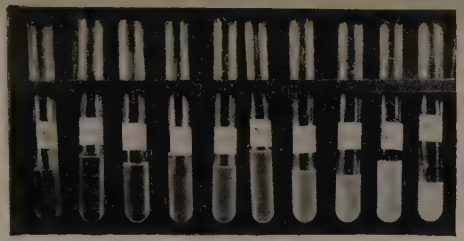

FIG. 1

FIG. 2

FIG. 3

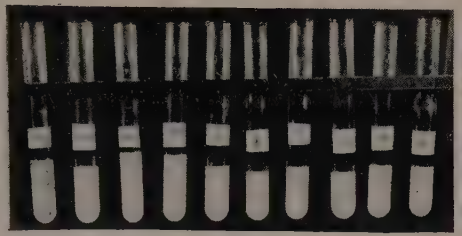

FIG. 4

FIG. 5

FIG. 6

The Periodic Opacity of Wassermann Antigen with progressively increasing Concentrations of Sodium Chloride.

FIG. 7

PLATE I

To face p. 30

substances—a network of α-gelatin whose spaces are filled with a structureless β-gelatin, and he [1] attributes the separation of foreign substances in layers to rhythmic changes in the structure of the network. Moeller [3, 4] draws conclusions as to the nature of the change from the spheritic structure of the deposits formed when hydrochloric acid diffuses into semi-liquid gelatin containing sodium chloride. Marriage made a study of the precipitated forms of lead iodide in various colloids and concluded that the nature of the colloid was of great importance in band formation. The interesting observation has been made by Burton and Bell that when gelatin, in which Liesegang rings are to be made, is allowed to set on a rubber sheet and then stretched, the ordinary effect is so modified that concentric ellipses whose major axes are in the direction of the stretching force, form by diffusion.

In view of experiments which will be described later, it does not seem feasible to entertain hopes of tracking the periodicity to the gel itself, but at the same time it is certain that the state of the gel has in many cases a strong influence in modifying the results. Liesegang [15] found that, in order to produce well-developed rings of silver dichromate, the gelatin should contain small quantities of acid and gelatose.* Normally, commercial gelatin contains sufficient gelatose through hydrolysis. Rings do not form unless this is present. In some instances, precipitation occurred in spirals instead of rings. Hatschek [7, 8] prepared rings of calcium phosphate by diffusing calcium chloride into sodium phosphate contained in a 10 per cent. gelatin gel. He found the acidity and gelatose content to be important factors in band formation and in certain instances obtained twin-rings and screw-like forms. In a further paper, Hatschek [9] describes attempts at a quantitative study of the rhythmic precipitation of lead chromate, and found the results to vary with different brands of agar, some specimens giving no bands at all.

Another interesting effect is the addition of foreign substances to the gel. Examples are cited by Holmes and by Koenig. According to the latter, alcohol decreased the distance between the bands of copper chromate, whilst sugar or glycerin caused the bands to be further apart. In some cases, spirals were obtained after addition of ethyl acetate. Foster [2] finds that the presence of traces of chlorides causes rings of silver dichromate to occur in groups of three instead of singly. To produce this effect it was only necessary to make up the gel with tap-water, which was known to contain a minute amount of chloride, in place of distilled water.

* Liesegang finds that gelatose increases the solubility of potassium dichromate in the gel (*Kolloid Z.*, 1907, **2**, 307).

The Ageing Effect.—The age of the gel also appears to be of importance and it is interesting to remember this in connection with some of the experiments of Hedges and Myers on the periodic dissolution of metals (Chapter IV). In the instance mentioned, the spacing in any one group of lines was dependent on the age of the gel before the diffusion was started. Foster [1] also observed that although ring formation occurred when the gel contained fresh colloidal copper, no rings formed if the colloidal copper were left for some hours previously. Liesegang [6] had already observed the influence of age on ring formation with silver dichromate. Koenig states that the best condition for band formation in silicic acid is a fresh gel, the bands becoming more and more irregular the longer the gel is kept before diffusion begins. Schleussner [1] states that a gelatin gel should stand for twenty-four hours before the experiment. Measurements by Blair show that the distance of the last ring from the centre of diffusion increases regularly with the age of the gel up to about thirteen days. Gels older than this lose their aptitude to form rhythmic structures, but appear to recover from this disability at a later period. In view of the doubtful past history of many colloids and the remarkable influence of foreign substances, including some of the products of reaction, it is not surprising that the observations of different investigators are not always in harmony. Such considerations make quantitative investigations very difficult.

Periodic Structures in Absence of a Colloidal Medium.—It is some relief from the individualistic properties associated with colloids to find that rhythmic structures of exactly the same type may be formed in absence of a gel. It should be borne in mind, however, that conditions have to be such as may very well exist inside a gel: it appears that such results are only realized when surface tension effects are given full play, by conducting experiments in capillary spaces or in very thin films of solution. Thus, Dreaper [1, 2] produced bands of many crystalline substances in absence of a gel by allowing the reacting solutions to interdiffuse through a glass capillary tube. Liesegang [20] has prepared banded precipitations in filter paper and Watanabe and Liesegang have obtained similar results in reaction media of kaolin, sand and pulverized calcium carbonate. Experiments by McGuigan and Brough show that rings of silver dichromate can be formed by placing a moistened silver nitrate crystal on a glass plate on which a thin film of potassium dichromate has been allowed to dry. Notboom obtained strata of lead iodide by the interdiffusion of lead nitrate and potassium iodide between a microscope slide and a cover glass, and under similar conditions

rhythmic banding of silver chloride has been observed by Brodersen. An interesting variation of this is the rhythmic deposition of precipitate from interacting gases. Koenig connected two litre flasks, containing respectively ammonia and hydrogen chloride, by a long, narrow tube. Bands of ammonium chloride appeared along the tube. A periodic deposition of sulphur was obtained when the flasks contained, respectively, hydrogen sulphide and chlorine. Karrer observed the formation of bands of ammonium chloride when two open cylinders containing ammonia solution and hydrochloric acid respectively were enclosed in a larger vessel, but he attributes this to a temperature gradient (compare Liesegang, p. 28).

The reactions which have been described in the preceding pages are often designated as " rhythmic reactions " or " periodic reactions." The writers consider that this term is misapplied, for there is nothing to suggest that the reaction time-curve is periodic. The final structure is periodic, but, whatever the explanation, it seems that the chemical action proceeds in a continuous manner. The writers, therefore, prefer to apply the term " periodic structures " to this type of periodicity and to reserve the term " periodic reactions " for those cases where it can be shown that the reaction velocity varies periodically.

Biological and Geological Illustrations.—Brief reference has been made to the interest of these phenomena in connection with the rhythmic structures so frequently encountered in biology and geology. Further examples of geological formations are given by Endell and by Tarr. Since it is known that light has a modifying influence in some cases, both Hatschek [9] and Davies [2] suggest that many naturally occurring rhythmic structures may be the result of alternating day and night rather than due to any inherent periodicity.

Some have sought to explain the so-called " fairy rings " in which moulds frequently grow on surfaces of agar, cheese, etc., in terms of rhythmic phenomena. The term " fairy rings " seems to have been applied originally in country parts to the rings of coarse, dark grass, which are often in evidence on pasture-land. According to Lawes, Gilbert and Warington,* the rich grass commences to grow on the debris of fungi springing up round a nucleus formed by animal excrement.

Liesegang[11] assumed that the iridescent film, formed when an alkali phosphate diffuses into a calcium salt contained in a gel, was indicative of a periodic structure. He showed that the film could be hardened by formaldehyde and discussed the possibility of the production of artificial pearls along these lines.

* *J. Chem. Soc.*, 1883, **43**, 208.

Küster [3] showed that the structure was not laminated and that the iridescence was due to the manner of folding of a delicate membrane. Liesegang [12] seeks to explain layered concrements such as gall-stones and urinary calculi on the same basis. Gebhardt traces the rhythmic markings on some butterflies' wings to this cause, and other biological examples are quoted by Lingelsheim. The annular markings of trees are related by some to Liesegang's rings. Jablczynski [2] has made measurements of the rings in agates and in tree-trunks and concludes that the former case is in complete accordance with the ordinary laboratory experiments in rhythmic precipitation, but the rings in tree-trunks do not fit in with the mathematical requirements. In certain directions, enthusiasm seems to have overstepped the bounds of caution. Surely, the rings in tree-trunks are the outcome of an external, seasonal periodicity.

Rhythmic Crystallization of Pure Substances.—It appears from the preceding pages that rhythmic structures may be produced by reacting solutions when the gel is replaced by conditions favourable to the display of surface-tension effects and also by crystallization of substances from gels in absence of chemical effects. It is not surprising, therefore, to find that many pure substances crystallize in waves from thin films of solution or the molten material. The rhythmic crystallization of thin films of sulphur from a melt was investigated by Fischer-Treuenfeld and by Köhler.[1] Vorländer and Ernst describe the concentric rings formed by crystals of 5-nitrophenyl-2-glycine-1-carboxylic acid from aqueous solution and the rhythmic crystallization of *p*-ethoxybenzylideneaminophenylpropionic acid from the molten state. This latter substance was the only one out of a large number investigated which exhibited this characteristic. It appeared that an air boundary was essential, for the waves were not developed when crystallization took place between two glass surfaces.

Alexéeff reports that molten ethyl ethanetetracarboxylate crystallizes in concentric zones when in thin layers and similar effects are recorded with supercooled benzophenone and coumarin. These effects are attributed to changes in the surface tension due to the heat of crystallization.

Rhythmic crystallization of inorganic salts from aqueous solution has also been realized, and the best-known case is that of potassium dichromate reported by Miers. This is effected by placing a drop of a saturated solution of the substance on a microscope slide and warming gently over a flame. The slide is then quickly transferred to the microscope. Crystallization commences round the edge of the drop and proceeds with a

little spurt and then stops: after a short interval the period of rapid growth starts again, producing branching figures, and this is again followed by a period of very slow growth during which a few large geometrical crystals grow. The periods should succeed each other at the rate of about five per second in order to obtain good rings. In general, the distance between the rings decreases with the thickness of the film of solution and with increasing rate of crystallization. Fig. 1 of the frontispiece is reproduced from a photograph of this effect (magnified 25 diameters) taken by one of the authors in Sir Henry Miers' laboratory. The view put forward by Miers is that crystallization of the first ring takes place by inoculation when part of the solution reaches the labile state by cooling: as soon as this rapid growth has reduced the concentration of the solution in the immediate vicinity to the metastable state, the crystals continue to grow slowly: in the meantime the next ring of solution is becoming labile by evaporation and cooling and the rapid crystallization recommences at some point. Such an explanation seems to meet the case of potassium dichromate, but it is doubtful whether its applicability is universal. It may be observed that the final effect is an alternation of a large number of small crystals with a small number of large crystals, thus bearing an analogy with Hatschek's observations on precipitated rhythmic structures. This alternating effect has also been observed by the authors [5] in the crystallization of thin films of chrome alum and of barium nitrate. A most interesting observation is that by the rapid cooling of thin films of chrome alum a metastable, birefringent, spherulitic form is produced: it is only when this metastable form has appeared that periodic crystallization has been observed. This fact suggests a link with other types of periodicity described later, which are associated with surfaces which are believed to be in a metastable condition.

Crystallization of sodium carbonate in concentric rings has been observed by Hofsäss. In these experiments, different forms of carbon were burned in oxygen and the combustion product was collected in N/10 caustic soda. The rings appeared under the microscope when one drop was taken and allowed to evaporate. They appeared in the absorption liquor only when graphite was burned. With other forms of carbon, dendritic forms resulted. It may be that some impurity, which has an effect on the surface tension of the solution, is responsible.

Kägi reports the rhythmic crystallization of the racemic menthyl ester of benzylacetic acid from solution in benzene or alcohol-acetic acid. Crystallization from ethyl acetate or from toluene was not periodic, and ring formation was not observed

under any conditions with the lævo-compound. The distance between successive rings, which is in most of these examples less than a millimetre, varied with the size of the drop and the concentration of the solution. Rhythmic crystallization of sulphanilic acid—sulphuric acid mixtures, *p*-tolunitrile, salol, and methylsalicylic acid has formed the subject of an investigation by Schubert, whilst Garner and Randall have shown that myristic, lauric, undecoic and decoic acids crystallize from thin films on surfaces of glass, silver, and certain crystal faces, in the form of waves. This does not appear to be a true case of periodic crystallization though, but due to the wrinkling of a skin which forms over the surface.

The foregoing instances are characterized by conditions where a small quantity of substance exhibits a large surface, but this does not appear to be essential for rhythmic crystallization. The present authors [5] have observed that benzoic acid crystallizes in a very beautiful wave-form from mixtures of sulphuric acid and ethyl alcohol. This effect is well portrayed in Fig. 2 of the frontispiece. It is not a surface formation, but affects the whole mass of substance, the layers being arranged round the crystallization nuclei like the coats of an onion.

This phenomenon can be reproduced by warming 5 gms. of benzoic acid with 12–20 c.c. of an equal-volume mixture of sulphuric acid and ethyl alcohol, and setting aside to cool. The crystallization starts from nuclei and spreads radially, with constant decrease in the distance between successive rings. Although in almost all cases of rhythmic crystallization the distance between successive rings is considerably less than a millimetre, in fact being observable often only by means of a lens, in the present case the effect is on a comparatively enormous scale and the rings in Plate I, Fig. 1, are about a centimetre apart. Examination shows the layers to consist of closely packed crystals of benzoic acid separated by spaces containing mostly solution with some benzoic acid crystals sufficient to give rigidity to the whole. Crystallization of benzoic acid from sulphuric acid or ethyl alcohol alone does not give rise to such periodic formations.

Periodic crystalline structures are not unknown in minerals and descriptions of periodic repetition by twinning in the amethyst and potassium chlorate have been given by Tutton, by Rayleigh,[1] and by Wood. The well-known interference colours associated with crystals of potassium chlorate appear to be the result of a fine laminated structure.

In addition to crystallization effects, periodic phenomena are to be observed in evaporation and condensation. Davies [3]

devised experiments in which strips of filter paper were suspended in solutions of various dyes. Coloured rhythmic bands appeared on the paper strips. West finds that when a hydrogen-oxygen mixture is ignited at the open end of a tube, water is deposited in bands along the tube. A striking wave-formation is often to be observed in clouds, generally on a summer evening when the vapours are in the act of condensing. The effect is sometimes quite transient, but often appears on a large scale with remarkable regularity.

CHAPTER IV

PERIODIC CHEMICAL REACTIONS

Hitherto our consideration has been of phenomena which are periodic with respect to some abstract variable and of structures which are periodic in form though they result apparently from a continuous process. The most important type of periodicity in many respects is a rhythmic time change and to this type belong all true periodic chemical reactions.

Theoretical Discussion.—It is of interest to note that mathematicians have provided for the existence of chemical reactions which may proceed in a periodic manner, but actual cases of chemical reactions satisfying the assumptions made have not been observed. For example, Lotka[1,4] shows that a series of damped vibrations must result when one of the products of three consecutive reactions catalyses its own rate of formation. Undamped vibrations must result when a substance A in constant concentration (maintained by using a saturated solution in presence of the solid) forms a substance B autocatalytically which in turn changes to a substance C autocatalytically. In such a case, the amplitude is dependent on the initial concentrations, but the period of vibration is a constant given by

$$T=\frac{2\pi}{\sqrt{ab}}$$

where a and b are velocity constants of the formation of B and C.

The same author [3] also shows that the rate of growth of a germ which feeds on the waste products of a certain species is oscillatory and points out the biological significance of this deduction. Other mathematical expositions of how an autocatalytic system may become periodic are given by Lotka [2] and by Hirniak.

Okaya [1, 2, 3] has attempted to apply a mathematical principle to Liesegang's phenomenon, the periodic catalytic decomposition of hydrogen peroxide by mercury and the periodic evolution of carbon monoxide from formic acid (*q.v.*). He makes the suggestion that the existence of quanta in natural phenomena is not limited to energy only. Hughes has made the suggestion

that a voltaic cell may be an electrical resonator responding to heat radiation of its surroundings and in which the electrodes act as valves, allowing current to pass in one direction only. He has made the further suggestion that if Armstrong's view that chemical reaction is reversed electrolysis is adopted it may be supposed that all chemical reactions will be periodic, and that if the circuits of the molecules are not in tune with the radiation they will exhibit " beats " which might appear as measurable periods. In such a system the rectifying action of the electrodes converts an oscillation into a one-sided pulsation such as is usually observed in periodic chemical reactions.

Cases of periodic chemical reactions have been reported at somewhat long intervals during the last century, but until quite recently no attempt has been made to find a general principle on which to account for the various cases. Generally, the isolated examples have been regarded as curiosities and have often been forgotten. A summary of the earlier cases has been made by Kremann.

These cases are sometimes reactions of an ordinary kind in which a product increases periodically in quantity, and there are also cases in which the effect is manifested in electrochemical terms. Although there is no fundamental difference between these types it has been considered convenient to treat them separately. Periodic electrochemical phenomena will therefore be discussed in Chapter VII, and here it is proposed to consider some of the reports of the periodic dissolution of metals in absence of applied current.

Early Experiments.—An early observation is that of Herschel from which it appears that iron wire dissolved in solutions of nitric acid up to a certain strength, but above this concentration iron went into a passive state and dissolution ceased. Using solutions of nitric acid intermediate in concentration between those required to render iron either active or passive, the metal was observed to alternate between the two states, gas being evolved in rapid pulsations of the order of several per second.

A better-known example is Ostwald's [2, 3, 4] research on the periodic evolution of hydrogen accompanying the dissolution of chromium in acids. The rate of the reaction was followed by employing a " chemograph " which registered automatically and continuously the pressure of hydrogen evolved. The first experiments with chromium showed that the rate of dissolution varied periodically and was accompanied by alternate periods of rapid and slow evolution of hydrogen, which Ostwald supposed to be due to alternating periods of activity and passivity of the

metal. It may be pointed out that the gas evolution did not cease and that therefore passivity in the usual acceptance of the term can hardly be held to account for the phenomenon. The forms of the periodic curves obtained varied with different specimens of the metal, but in any one case the frequency was determined by the conditions of the reaction. The frequency increased with increasing concentration of acid and also with rise in temperature, being approximately doubled by each rise of 10° C. Remarkable effects were observed to result from the addition of small quantities of foreign substances, traces of formaldehyde and potassium cyanide being sufficient to diminish the frequency enormously and even to stop the " waves " altogether. Under similar experimental conditions periodic phenomena were not observed in the dissolution of zinc, iron or manganese in acids.

A most important observation made in this work is that when the particular batch of chromium was used up, no periodic results could be obtained from other specimens, the gas evolution on dissolution being quite steady. Ostwald [3] complains in the following words : " Diese ergeben keine Schwingungen so dass es aussah, als wenn meine weiteren Untersuchungen ein vorzeitiges Ende nehmen müssten, da nur wenige Gramme der ursprünglichen Probe übrig geblieben waren." Determined attempts were made to render the metal periodically active by different forms of previous treatment. The following are mentioned as being ineffective : addition of cuprous chloride, sodium sulphite, alcohol, ferrous chloride, ferric chloride, colloidal platinum, chromic acid, potassium nitrite ; contact with metallic platinum, variation in temperature between 0° C. and 50° C., treatment of the metal with chromic acid or potassium permanganate, fusion with potassium nitrate, heating on charcoal with sodium phosphate with a view to adding phosphorus, melting in an electric furnace in an atmosphere of coal-gas, using the metal as anode. Fortunately Goldschmidt was able to provide a further small supply of the original batch of metal and this enabled Ostwald to show that a periodic E.M.F. was given by the cell Cr(periodic)/HCl/Pt. More detailed measurements of the electrical effect were made later by Brauer.

Interesting observations were made with one specimen of chromium which contained 0·13 per cent. of sulphur and which was designated Cr 13. This specimen dissolved quite readily in acids when alone, but when crushed and tied up in a muslin bag, periods were obtained. This result was shown to be due to a minute amount of some substance obtained from the fabric and could be brought about without the use of the bag. Thus

Cr 13 dissolved periodically in hydrochloric acid containing small quantities of starch or dextrin, these being effective when present to the extent of only 0·001 per cent. Ostwald then proceeded to make a study of the effect of adding a large and miscellaneous assortment of substances ranging from colloidal silica to beer. As a result, it was concluded that periodic properties were induced in Cr 13 by the addition of carbohydrates of high molecular weight, and since inorganic colloids were without action it was not regarded as a colloid property. Ostwald was of opinion that the periodicity was due to some impurity contained in the original batch of chromium. The samples were known to contain small quantities of silicon, carbon and sulphur, but it was not discovered to which, if any, of these the phenomenon was to be attributed. Wullf suggested that the secondary waves to be seen in many of the curves were connected with the two forms in which chromium salts are known to exist. Döring found that on dissolving chromium in hydrochloric acid the immediate product was chromous chloride which later became chromic chloride, the latter reaction being catalysed by silica and many other substances. He supposes that the periodic effects observed by Ostwald are due to the interference of these two reactions.

Other cases of periodic dissolution of metals are given by Banerji and Dhar, who observed in the dissolution of a 50 per cent. iron-nickel alloy in 20 per cent. nitric acid four or five irregular periods separated by intervals of no reaction, and by Desch, who mentions the periodic dissolution of a 10·5 per cent. chromium steel in nitric acid.

The Periodic Dissolution of Metals.

It is now proposed to give an account of the work of the present authors [1, 3] on the periodic dissolution of metals with a view to making clear that the phenomenon is a general one under certain conditions. The general method of experimentation employed was to conduct the reactions in an apparatus as shown in Fig. 2, and either to record automatically the pressure of gas evolved by tracings on smoked paper, or to measure it directly by means of an aniline manometer. As will be seen in the sketch, a leak was provided in the form of a length of thermometer tubing so that though the gas could escape it was held sufficiently long to show marked pressure changes. This apparatus is a modification of Ostwald's "chemograph."

The following reactions have been found to be periodic under certain conditions: the dissolution of zinc, iron, aluminium,

manganese and cadmium in hydrochloric acid ; of zinc and magnesium in sulphuric acid ; of aluminium and magnesium in orthophosphoric acid ; of calcium, sodium amalgam and aluminium amalgam in water ; of magnesium and zinc in ammonium chloride solution ; of aluminium in cupric chloride solution ; of magnesium in nitric acid ; of magnesium in acetic acid ; of sodium in ethyl alcohol ; of sodium in *n*-butyl alcohol ; of aluminium in solutions of caustic soda, barium hydroxide and potassium carbonate ; of copper, nickel, cobalt, iron in mixtures

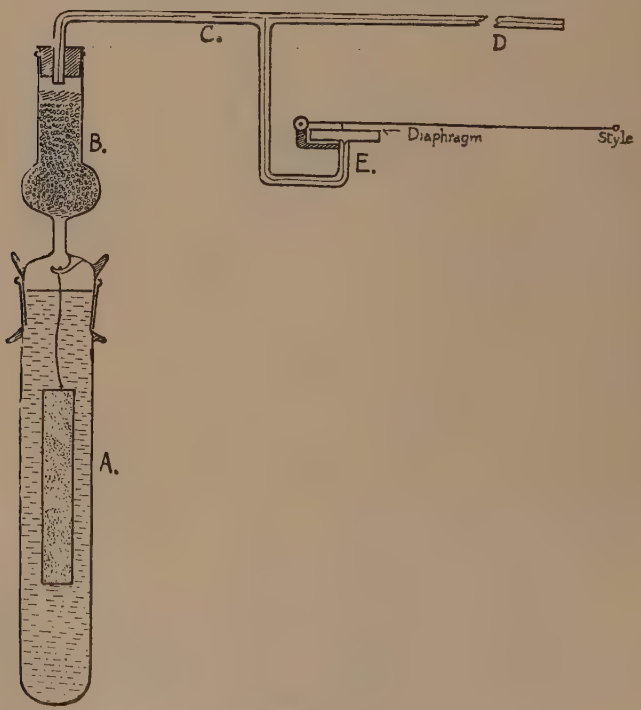

Fig. 2.

of hydrochloric and nitric acids of certain compositions, and the evolution of hydrogen by the autoxidation of chromous chloride solution in presence of platinum. These reactions do not, in all probability, exhaust the cases of periodic chemical reactions of this type.

The following reproductions of the automatically recorded " waves " are interesting as showing various features of these periodic systems. In considering them, it is necessary to remember that the recording apparatus possesses a certain " lag " which

leads to the "wave" appearance. The increase in pressure is developed much more quickly than these records suggest, and the graphs (which will be given later) prepared by plotting direct-pressure readings taken at intervals of 15 seconds give a more accurate impression.

The records shown in Fig. 3 represent in each case a time interval of eight and a half minutes.

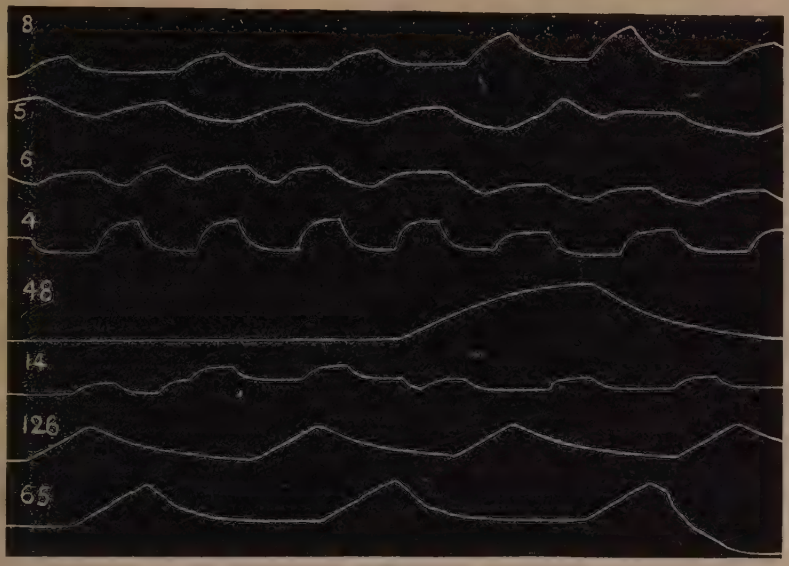

Fig. 3.

References to Fig. 3.

No. 8. Manganese in 0·3 *N* hydrochloric acid.
No. 5. Iron in 3 *N* hydrochloric acid.
No. 6. Zinc in *N* hydrochloric acid.
No. 4. Aluminium in 3 *N* caustic soda.
No. 48. Aluminium in 0·3 *N* baryta.
No. 14. Aluminium in 2 *N* caustic soda.
This record exhibits the not unusual feature of secondary waves. Tertiary and even quaternary waves have been observed.
No. 126. Aluminium in 2 *N* hydrochloric acid.
The experiment which furnished this record was followed for twenty-two hours, during which time it was periodic.
No. 65. Aluminium amalgam and water.

Figs. 4 and 5 have been prepared from direct readings of the pressure and the following features will be observed:

1. The frequency of the periodicity decreases throughout the

course of the reaction, and in this case the form of the graph suggests that the periodicity existed at a much higher frequency before it was revealed by the measurements. In many cases, however, something of the nature of an induction period is shown by both graphs and records before periodic properties are observed.

2. The periodic property consists of sudden increases in the rate of reaction and not of alternate periods of activity and passivity of the metal.

3. The pulses are superimposed on the ordinary reaction curve

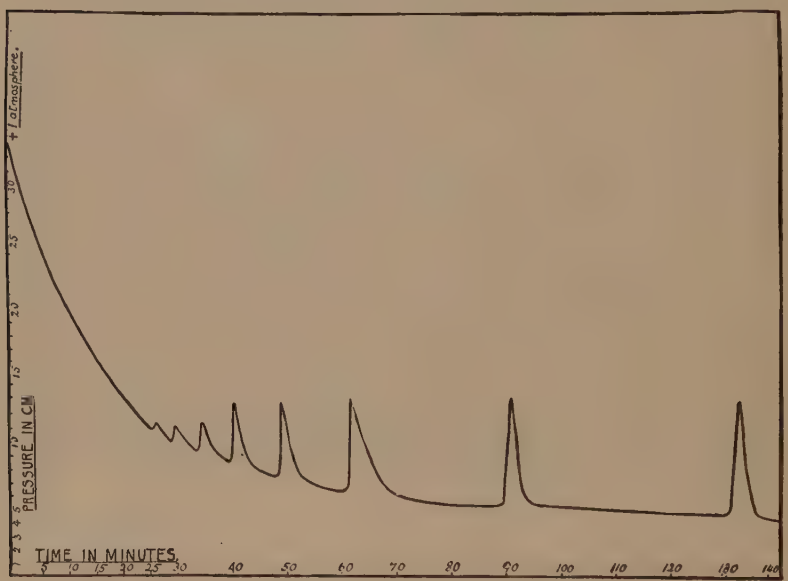

Fig. 4.—Aluminium + N.HCl at 35° C.

and suggest that the reaction is being catalysed at definite intervals of time.

The Activating Agent.—The authors did not escape the bugbear of work on periodic phenomena, viz. failure to be able to repeat at will a given observation even when the conditions are apparently identical. All the cases to which reference has been made (Fig. 3) were carried out in a large test-tube which was in use for several weeks, but whose previous history was unknown. After many successful experiments it was observed that no matter what system was being examined the periodic phenomenon was becoming less and less marked and finally died out altogether. Exhaustive experiments led to the conclusion that

the vessel possessed originally an inner surface which was essential to the periodicity, but it was not found possible to identify what substance other than glass had formed that surface. It may be remarked, however, that it has been found possible to produce " naturally active " vessels (in which reactions are periodic without the addition of any external agent) by various means. Such effects have been realized by soaking vessels in lead acetate solution for ten months or in a mixture of colloidal platinum and gelatin for three months.

Special experiments with chromium showed that this metal behaved like all the others, being periodic only in " active " vessels or in the presence of other components which have come to be regarded as activating agents. These experiments with

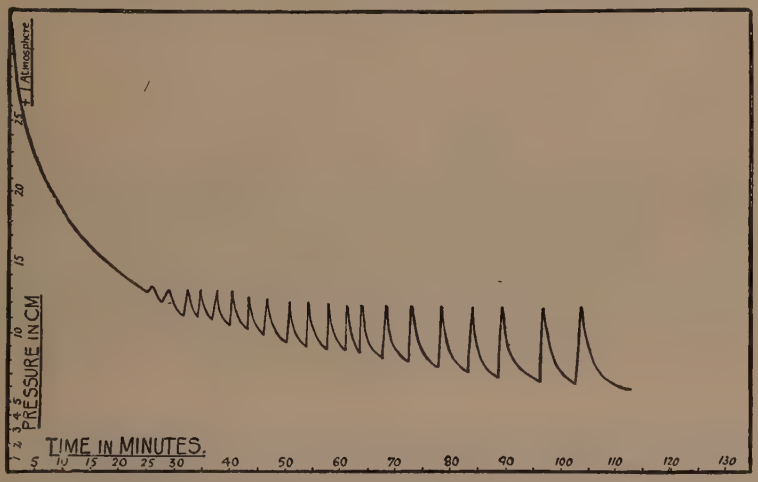

Fig. 5.—10 per cent. Sodium Amalgam + Water at 35° C.

chromium demonstrate that the Ostwald case is one example of what is now shown to be a general phenomenon affecting most metals. There is, however, one difference between Ostwald's chromium experiments and the systems here described. The periodicity in Ostwald's case was in all probability induced either by a constituent of the chromium or by the condition of the metal, whereas in the present authors' early experiments the active agent was obtained from the vessel. Thus, Ostwald observed that two pieces of chromium dissolving together, but not in contact, in hydrochloric acid gave a double summation curve, whilst in the present experiments any number of pieces of metal could be used simultaneously without changing the form of the waves.

After the original active vessel had failed, many devices (*loc. cit.*) were employed to revive the periodicity with indifferent success until it was discovered that substances of a colloidal nature could sometimes induce the periodic dissolution of a metal. Record 74 (Fig. 6) was obtained in presence of gelatin; No. 61 was given by colloidal lead; Nos. 80 and 87 are typical results from gamboge and colloidal antimony sulphide respectively. No. 94 shows the tracing of an experiment with aluminium amalgam and water in presence of "Night Blue." In this case the vessel was treated for some hours with a 0·1 per cent. solution of the dye and after rinsing was used for the reaction.

Although it was eventually found that though colloidal substances had a marked effect on the phenomenon, they were not entirely reliable, certain important conclusions may be drawn from the positive results:

1. Numerous experiments showed that the phenomenon was

Fig. 6.

only observed with freshly prepared colloids. They were frequently ineffective after standing a day.

2. The quantity of the colloid necessary was extremely minute. Gelatin was never used in a concentration higher than 1 part in 100,000, and albumin ten times less than that.

3. The effect could often be obtained either by soaking the vessel or the metal in the colloid, in which case the final concentration of the colloid in the system must have been excessively small.

The next development of the work was the observation that in certain vessels the colloids were active whilst in others they were not, and it was eventually found that, in presence of a suitable colloid, periodicity could always be relied on in a platinum vessel or if a piece of platinum were present. Gold and palladium were also effective in this respect in place of platinum. Records 99 and 100 (Fig. 7) were obtained in presence of gold and platinum respectively, together with gelatin.

It therefore appeared that both a colloid and a "second metallic component" were necessary for the periodic dissolution of a metal and it was first established that any dissolution of the second metal was not the decisive condition.

Methods of Activation.—Such a complex system was not regarded as a hopeful field of work, and in trying to simplify it it was found that the colloid might be dispensed with if the second metal was "activated." This was brought about in a variety of ways, including successive heating and cooling in a vacuum; using the metal in a chemical reaction so as to affect

Fig 7.

its surface; bombarding its surface with cathode rays; cold-working its surface by rubbing or scraping, or better by cold-rolling; electro-deposition at high current densities. By one or other of these methods it was found possible to activate platinum, palladium, gold, silver, copper, chromium and iron for the purpose of acting as second metallic components in a periodic reaction. Mercury was found to need no process of activation.

Record 130 (Fig. 8) was obtained from cadmium in hydrochloric acid in presence of platinum, the activation of the platinum

Fig. 8.

being accomplished in this case by cathode ray bombardment. No. 125 shows the periodic dissolution of magnesium in 10 per cent. ammonium chloride solution in presence of copper which had been heavily scraped.

Similar results were obtained from alloys of copper and aluminium after the alloy had been melted in air.

The vacuum-heat treatment of metals for this purpose was not so satisfactory as some of the other methods. It appears probable that its effect can only appear if the metal originally contained absorbed gases. The driving out of these gases will no doubt

upset the surface and produce the metastable condition which seems to be the result of all the methods of activation.

An experiment was devised to demonstrate that in these two component systems the seat of the periodicity was not the dissolving metal but rather the second component. Platinum causes the evolution of hydrogen from a solution of chromous chloride, the salt undergoing oxidation. This may be regarded as a decomposition of water by chromous chloride in presence of platinum as a catalyst. It was found that if ordinary platinum was used the gas evolution was quite regular, whilst a well-developed periodicity appeared on using activated platinum. This experiment is important in that it shows that the periodic phenomenon is independent of the dissolving metal.

Other satisfactory methods of preparing periodically active two component systems are by the electrolytic or chemical deposition of the activating metal component. The dissolution of magnesium in 0·2 *N* hydrochloric acid can be rendered periodic by putting the metal in contact with a piece of copper, which has been used as cathode in an electro-depositing system consisting of two pieces of inactive copper, in a 20 per cent. solution of copper sulphate with 5 per cent. sulphuric acid and employing a current density of 6·25 amps. per sq. dm. The deposition was continued for twenty minutes and it was found that the high current density was advantageous for the production of well-marked periodicity. Record No. 142 (Fig. 9) shows the tracing of this experiment. It is of interest to note that the anode of the cell also proved to be an active second component, but its activity soon died out.

The system magnesium-hydrochloric acid has also been rendered periodic by depositing on the magnesium various metals by chemical action. Record 143 (Fig. 9) was obtained after dipping the magnesium in 0·1 per cent. copper sulphate solution for five minutes, and No. 147 by using dilute stannous chloride solution. No. 143 has a special interest in demonstrating the importance of the second metal. The periodicity will be seen to stop suddenly and it was observed that at this point the copper film slipped off the dissolving magnesium. The same system has been rendered periodic by the metallic deposits resulting from the addition of cupric chloride, bismuth nitrate (No. 148), stannous chloride (No. 146), antimony chloride (No. 149), and ferrous sulphate (No. 150). Galecki and Kuczyński also note the observation of periods in the dissolution of zinc in acid solutions of copper sulphate.

Frequency.—After examining the various examples which have been shown one is struck by the great variation in frequency

among the different cases. In comparing the frequencies one of the greatest differences among those shown is to be seen in the cases of No. 48 (Fig. 3) and No. 29 (Fig. 10), but though the difference here is great there is no reason to doubt the possibility of frequencies both higher and lower than these. The maximum duration of a wave which has been observed is two hours and the minimum is ten seconds.

Experiments on a given system have shown that the frequency is dependent on various factors. Among these may be mentioned the concentration of the reagent, the temperature and the amount and condition of the activating material. The influence of the concentration of the reagent may be deduced by reference

Fig. 9.

to Figs. 4 and 5, but quantitative measurements on series of experiments with aluminium and caustic soda varying in concentration from 0·5 *N* to 4 *N* have shown definitely that the frequency varies directly with the concentration of the reagent. Reference has already been made to the influence of temperature, which was measured by Ostwald.

In regard to the effect of the second component it has been observed (Hedges and Myers [3]) that low-frequency waves are produced by a large deposit of copper on magnesium in the systems recently discussed, whilst a thin film gives rise to a higher frequency. Similar results were obtained in the case of electro-deposited copper, though in this case the copper was

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not deposited on the magnesium. Experiments with copper-aluminium alloys of varying composition have led to the same result. The frequency of the periods can be diminished very greatly by the addition of small amounts of formaldehyde, potassium cyanide or sodium arsenate, and larger quantities of the "poison" stop the periods altogether. Record No. 82A and B (Fig. 9) shows how the frequency of the system aluminium amalgam-water was diminished by the addition of 0·8 per cent. formaldehyde, and No. 132A and B shows a similar effect on the frequency of the system aluminium-copper alloy dissolving in 3 *N* hydrochloric acid by the addition of 1 per cent. sodium arsenate. In some of the systems examined the addition of 1 per cent. potassium cyanide reduced the frequency to one-fiftieth of its former value.

Chloroplatinic acid has a remarkable toxic effect on some

FIG. 10.

systems, one part in a million being sufficient to inhibit the production of waves. Incidentally, chloroplatinic acid has been observed to exert a strong catalytic effect on the dissolution of many metals in hydrochloric acid. In the case of aluminium a concentration of chloroplatinic acid so small as 10^{-9} produces an increase in the rate of dissolution of more than 20 per cent.

Autoperiodic Reactions.—Hitherto, the cases of periodic dissolution of metals appear to depend not so much on the nature and condition of the dissolving metal itself as on some additional factor. Cases have been quoted in which the active agent appears to have been on the surface of the vessel, in other instances colloidal substances have apparently been responsible, and in yet others the presence of a second metal in a particular condition has led to periodicity.

A consideration of the state of the second metal in its active form has led (Hedges and Myers [4]) to the preparation of systems

which have been examined for the sake of convenience electrochemically, which are periodic without, as far as is known, the addition of any other component. It has been found possible to activate copper, for instance, by methods similar to those used in activating the second components, and so the systems have been rendered simpler from the point of view of theoretical treatment.

Supersaturation.—With a view to clearing the ground to some extent, it will be well to discuss here the question of some form or other of supersaturation as a basis for the interpretation of these periodic phenomena. It is at once apparent that where a gas is being evolved from a solution supersaturation becomes a possibility and in certain instances might lead to periodicity. In fact, Findlay and King have shown that if gelatin or dextrin solutions are saturated at high pressure with carbon dioxide, the gas is evolved periodically after the pressure is released

In the present cases, it is considered that supersaturation plays no part for the reasons stated below. The phenomenon does not consist of an intermittent evolution of gas, and except in

Fig. 11.

the case of a few of the slower reactions the rate of disengagement of the gas is sufficient to render the contents of the vessel in a continuous state of foam. There can hardly be supersaturation of the liquid phase under these conditions. Again, periods are still obtained when the inner surface of the reaction vessel has been ground with carborundum powder. The addition of finely divided substances such as barium sulphate, carbon or platinum black does not interfere with the phenomenon and no alteration is produced by agitation of the vessel. The existence of secondary and tertiary waves is hardly consistent with a supersaturation view.

Further, in regard to the metal itself, if this be made the anode of an electrolytic cell, periods are obtained, but if the current be reversed the gas evolution becomes quite regular. One experiment on this question may be quoted. A cell was constructed which had one electrode of aluminium and the other of platinum wire, the reagent being 3 *N* caustic soda. The metal was first allowed to dissolve without passing any current, and Record No. 69 (Fig. 11) shows the tracing of the gas pressure. The aluminium was then made the cathode and immediately the

evolution became and remained perfectly regular, the record consisting of a straight line. It is to be observed that in this case the metal does not dissolve but the gas comes from the aluminium. When the current was reversed, making the aluminium the anode, the waves recommenced (No. 70). In this case the metal dissolves, but the gas does not come from the aluminium. It is clear, therefore, that supersaturation of the solution or of the metal with gas plays no part in the phenomenon.

CHAPTER V

THE PERIODIC CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

The periodic phenomena accompanying the dissolution of metals under certain imposed conditions appear in every case to be the result of a periodic influence of a secondary agent on the dissolving metal. This secondary agent, in that it affects the velocity of the change but remains unaltered itself, may be regarded as a catalyst, and the general phenomenon may therefore be considered as the periodic catalysis of a normal reaction. In the periodic evolution of hydrogen by the autoxidation of chromous chloride in presence of activated platinum, a separation of the periodic catalysis from the normal reaction has been realized, for, in this case, the metal does not undergo dissolution and the whole of the reaction may be regarded as catalytic.

It may be inferred from these considerations that other instances of periodic catalysis involving no reaction apart from the catalytic effect might be observed when such activated metals or other substances were placed in contact with solutions which they decomposed catalytically. An obvious example, well suited to experimental investigation, is the catalytic decomposition of hydrogen peroxide.

Solutions of hydrogen peroxide are decomposed at a convenient speed by some of the metals which have been used as second metallic components in other systems, and it was anticipated, therefore, that some of these metals might, after suitable treatment, decompose hydrogen peroxide periodically. Special interest is attached to such purely catalytic systems in consequence of the well-known observation by Bredig and Weinmayr of the pulsating catalysis of hydrogen peroxide by mercury. Mercury, it may be remembered, is the one metal which appears to require no activation in the systems involving the dissolution of a metal, and that this metal should decompose hydrogen peroxide in a periodic manner is strongly suggestive of a common origin to which the periodicity of such apparently diverse systems may be traced.

Mercury as a Catalyst.—The first observations of Bredig and Weinmayr were made by titrating 1 per cent. hydrogen peroxide, kept in contact with mercury, at regular intervals of

time with potassium permanganate solution. The titration curve was sinuous. Later, the observation was made that when 1 c.c. of pure mercury contained in a tube was covered with 10 c.c. of 10 per cent. hydrogen peroxide, the evolution of oxygen was visibly periodic. The oscillations were followed on a small manometer and varied from one to twenty per minute under different conditions. Concurrently with the periodic evolution of gas appeared an alternating change at the surface of the mercury, the surface becoming periodically covered with a golden film. The active periods of evolution of gas took place each time the golden oxide film dissolved, leaving the mercury surface bright. Periodic changes in the potential of the mercury with respect to the solution and in the surface tension at the mercury surface formed a further accompaniment to the rhythmic evolution of oxygen. The E.M.F. of the cell constructed by coupling up this system to a standard calomel electrode was 0·254 volt during the active periods and 0·322 volt during the inactive periods. In the latter case, when the film was reinstated, the mercury meniscus was observed to flatten perceptibly. The frequency of the periods increased during the reaction and underwent a marked increase with rise of temperature. Addition of acid or alkali and many salts inhibited wave-formation.

The conditions determining the appearance of this periodic effect were more closely investigated by Bredig and Wilke.[1] As appears to be so often the case in periodic phenomena, they found the course of events to be altered considerably by the presence of substances in quite small quantities. The best results were obtained when the hydrogen peroxide solution contained 10^{-3} to 10^{-4} gram molecules of alkali per litre, and the inhibitive effect of sodium chloride was perceptible at a dilution of $0{\cdot}000002N$. In the normal way, this small amount of alkali was obtained from the glass vessel after a time and it was observed that, unless the alkali was added directly, the pulsations did not commence as a rule until several hours had elapsed. The periodicity was still apparent when the mercury was anodically or cathodically polarized. Later, Bredig and Wilke [2] found it possible to regulate the pulsations in such an experiment, employing either an alternating or a direct current.

Nernst has shown that in physiological systems there is a quantitative relation, between the strength i of the alternating current required to produce a certain stimulus and the frequency n of the current, represented by $i/\sqrt{n} = k$, where k is a specific constant depending on the particular system. The observations of Bredig and Kerb show that this relation holds throughout the

range of frequencies possible in the catalytic decomposition of hydrogen peroxide.

This example of periodic catalysis was investigated more intimately by Antropoff,[1] who employed self-registering instruments which recorded simultaneously the rate of evolution of oxygen and the potential difference existing at the mercury-hydrogen peroxide interface. Addition of sodium acetate, followed if necessary by acetic acid, appeared to be a useful means of adjusting the alkalinity of the solution to within the required limits. In conformity with the observations of others, Antropoff found that quite minute quantities of other substances exerted a profound influence on the course of the phenomenon. So important was this factor that a routine method of cleaning the reaction tubes had to be adopted, for the treatment of the tubes affected the experiments conducted in them thereafter.

Both Fredenhagen [2] and Antropoff trace the periodic catalysis to the oxide film which is observed to form periodically over the surface of the mercury. The former bases his proposed mechanism on the idea of supersaturation with oxygen at the mercury surface, with formation of an oxide film which would normally be unstable. At a certain degree of supersaturation the imprisoned oxygen escapes in some haste, leaving the oxygen pressure below the dissociation pressure of the unstable oxide, which therefore decomposes. The whole cycle is then renewed. Antropoff, however, from observations under the microscope concluded that the film disappears by dissolution and not by reduction, the evolution of oxygen occurring at the metal-film boundary. He advanced the view that the oxide film formed over the mercury surface breaks through mechanical strain and at the point of rupture a local electrolytic circuit is set up, the metallic mercury acting as cathode and the oxide film dissolving anodically.

The composition of the oxide film has been discussed by Bredig and Antropoff and has been the subject of a special study by Antropoff.[2] It does not appear to be very definite, however, for the films observed by Lemoine, using more concentrated solutions of hydrogen peroxide, were much darker in colour, bordering on to black. This matter is of some importance, for the alternate appearance and disappearance of the film has been quoted by Bancroft [2] and others in support of the intermediate-compound hypothesis of catalysis.

Experiments by Hedges and Myers,[2] however, tend to show that the periodic formation of the oxide film is to be regarded as a concomitant effect rather than as a cause of the phenomenon, for the formation of the film has been observed under conditions

when the evolution of oxygen was not periodic, and a periodic evolution of gas has been observed in presence of gelatin when no visible film formed over the mercury. Indeed, it would seem that the periodicity is of a more fundamental nature than has been supposed hitherto, for periodic decomposition has been realized with several other catalysts.

Other Metal Catalysts.—In these experiments, 20-volume hydrogen peroxide was used throughout, the reaction mixture being kept at 35° C. The course of the decomposition was followed by taking readings every fifteen seconds on an aniline

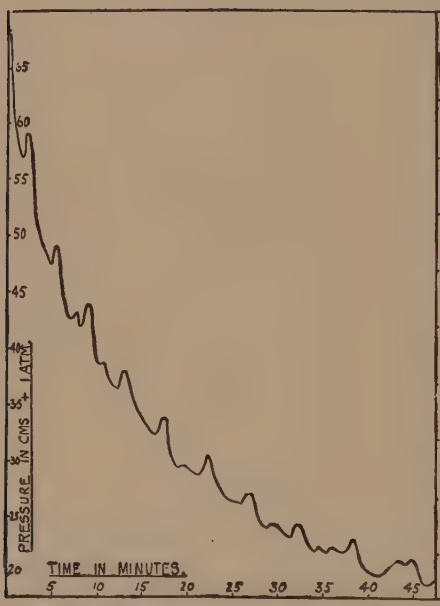

FIG. 12.—Periodic Decomposition of H_2O_2 by Silver at 35° C.

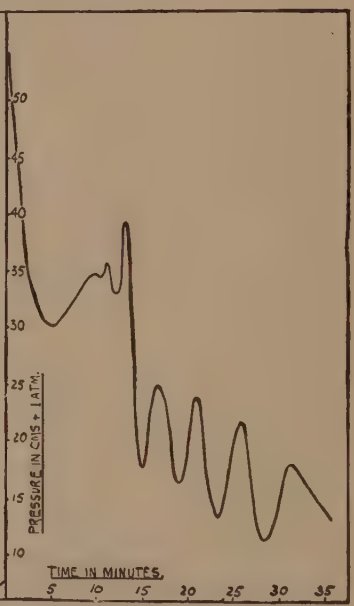

FIG. 13.—Periodic Decomposition of H_2O_2 by Magnesium Amalgam at 35°.

manometer coupled to the apparatus described in Chapter IV. A periodic rate of decomposition has been obtained with finely divided copper and silver prepared by certain methods, although finely divided platinum, iron or cobalt gave negative results even after vacuum-heat treatment. Fig. 12 shows the periodic decomposition of hydrogen peroxide by silver reduced by means of hydrazine sulphate.

Certain metallic couples and alloys were observed to decompose hydrogen peroxide periodically when the nobler metal was activated by suitable treatment. Periodic curves were also

obtained using metals dissolved in mercury. For instance, although mercury was observed to decompose neutral hydrogen peroxide very slowly, a rapid and periodic evolution of oxygen ensued on dropping a piece of aluminium on to the surface of the mercury. Similarly, the periodic curve depicted in Fig. 13 was obtained by acting on hydrogen peroxide with a liquid amalgam prepared by dissolving magnesium in warm mercury.

A negative result was obtained with coco-nut charcoal before and after vacuum-heat treatment, although Firth and Watson describe irregularities in the rate of evolution of oxygen from hydrogen peroxide when decomposed by pure sugar carbon which had suffered heat treatment in a vacuum.

Colloidal Catalysts.—Success has also been achieved by Hedges and Myers [2] using colloidal catalysts. Among these are catalase, colloidal silver and colloidal platinum. In these instances, the ageing phenomena described in the colloid systems involving the dissolution of metals were again in evidence, for, after standing for some days, these colloids were found to produce a smooth reaction curve. Analogous cases of periodicity in enzyme action and in other colloid catalysts are described in Chapter VI. Periodic decomposition curves were also obtained with some freshly prepared metallic oxides. Among these were cupric oxide, cuprous oxide and barium dioxide.

One of the few cases of periodicity in a homogeneous system is reported by Bray in studying the decomposition of hydrogen peroxide by iodine. The reactions involved are

(1) $5H_2O_2 + I_2 = 2HIO_3 + 4H_2O$,
(2) $5H_2O_2 + 2HIO_3 = 5O_2 + I_2 + 6H_2O$,

and the reaction

(3) $H_2O_2 = H_2O + \frac{1}{2}O_2$, which takes place concurrently and is catalyzed by the iodine and iodic acid. In presence of certain concentrations of sulphuric acid a slow periodic decomposition of the hydrogen peroxide occurs and this is accompanied by a periodic darkening of the solution by free iodine. According to Bray, the reaction is strictly homogeneous, for the oxygen does not form bubbles, but slowly diffuses out of the solution. By the direct addition of iodine to hydrogen peroxide, the present authors observed irregularities in the rate of evolution of oxygen, but it is believed that this was a supersaturation effect due to the homogeneity of the system, for, when the system was made heterogeneous, as in the other cases investigated, by addition of finely divided solid matter, the decomposition followed a steady course.

A most interesting announcement has been made by Ditman,

who claims to have effected catalytic action at a distance. Separate tubes containing colloidal platinum (or other catalyst) and hydrogen peroxide solution respectively are connected by means of a metallic conductor, and decomposition of the hydrogen peroxide is said to result. If in this conductor is inserted the primary circuit of an induction coil and a wire is led from the secondary circuit terminal to another tube containing hydrogen peroxide solution, then decomposition occurs also in this tube at a greater rate than in the tube connected with the primary circuit. This suggests that there travels through the primary circuit an intermittent or oscillating electrical impulse. The present authors have repeated Ditman's experiments, using metals which do not of themselves decompose hydrogen peroxide, but have been unable to confirm his observations. Prior to publication of these results a paper appeared by Davey, refuting the claims of Ditman.

Other Periodic Catalytic Systems.—The decomposition of hydrogen peroxide by activated substances was investigated because this is such a clean reaction, the products being water and a gas which is removed from the sphere of action. It may be anticipated, however, that in addition to this reaction and the evolution of hydrogen from solutions of chromous chloride, other (though not necessarily all) catalytic decompositions by such agents might follow a periodic course. There are in the literature a few records of irregular variations in reaction velocity in such instances.

Paal and Hartmann, and Paal and Schwarz studied the rate of combination of hydrogen and oxygen in presence of colloidal platinum and colloidal palladium. The experiments were carried out at room temperature in a gas burette which was connected with a shaking apparatus. The curves given in these papers show marked irregular deviations, although these investigators do not pay much attention to the fact.

Experiments on the rate of combination of hydrogen and oxygen in presence of platinum black before and after heat treatment have been made by the present authors. The experiments were conducted at 35° C. by leading electrolytic gas into an evacuated vessel containing the catalyst and immersed in a thermostat. A three-way tap attached to the reaction vessel permitted of subsequent connection of the system to a manometer on which the rate of change was followed. A mercury manometer was used at first, and later, in order to obtain more delicate measurements, a long manometer containing pump oil of low vapour pressure was employed. In no case was a suggestion of periodicity observed, all the curves obtained being smooth.

Very irregular reaction curves are given by Lush for the rate of hydrogenation of various oils by a nickel catalyst.

To so great an extent does periodicity in chemical reactions appear to be associated with either pure catalysis or a superimposed catalysis that the suggestion is inevitable that catalytic action itself may be dependent in some way on this principle. Experiments (see Introduction) show that in some instances a pulsating effect is more efficient than continuous action, and, indeed, such a principle is unconsciously employed continually in everyday matters. For example, when any mechanical or even moral obstacle has to be overcome, it seems more efficacious to apply alternate periods of constraint and rest rather than a continuously increasing restraint.

It may be that in such a view is to be found the explanation of the ease with which reactions proceed in presence of a catalyst, though at present there is not enough evidence to make this anything more than a mere suggestion. At the same time, it is quite possible that all catalysis is periodic in character, though it is only in such cases as have been investigated that the effect is of such magnitude or frequency as to be capable of detection by the methods employed.

CHAPTER VI

MISCELLANEOUS PERIODIC REACTIONS

The Periodic Luminosity of Phosphorus.—Of the few reactions, in addition to those which have already been described, in which periodicity has been observed, the intermittent glow exhibited by phosphorus under certain conditions has received the fullest investigation.

The first mention of this phenomenon appears to have been made by Munck af Rosenschöld in 1834, but systematic observations were not undertaken until forty years later, when Joubert made a study of the conditions under which the glow of phosphorus is to be observed. Joubert observed that when a vessel containing glowing phosphorus was evacuated, the glow was extinguished ; below a certain pressure, however, and before the stage of extinction, the luminosity became intermittent. Further observations were made by Centnerszwer and later by Bloch.

A more thorough investigation was undertaken by Rayleigh.[3] An apparatus was arranged in which phosphorus was melted into position in a wide horizontal tube closed at both ends but provided at intervals along the length with open vertical capillary tubes allowing the slow entrance of air to take the place of the oxygen consumed by the phosphorus. Gradually the atmosphere inside the apparatus became richer in nitrogen and below a certain partial pressure of oxygen luminous pulses were observed to travel along the tube. The presence of water appeared to be necessary for the appearance of these pulses and the periodic luminosity normally disappeared slowly as a result of desiccation by the oxide of phosphorus. The intermittent glow could be restored by adding a few drops of water. In place of water, camphor, nitrobenzene, butyl alcohol, amyl nitrite, oil of bitter almonds and ammonia could be used successfully. Turpentine was observed to prevent the glow altogether except when in minute quantities which permitted periodicity. Rayleigh supposed that the propagation of the glow is analogous to an explosion wave and that nuclei are necessary for this to start. The nuclei may be formed from the combustion product and it is supposed that an inhibitor takes prior possession of them. This action is in time overcome by the formation of an increasingly favourable oxygen-phosphorus vapour mixture. On the

other hand, Weiser and Garrison attribute the intermittent glow to the periodic breaking of an unstable oxide film.

Waran has observed the intermittent luminosity under conditions rather different from those of Rayleigh's experiments and concludes that Joubert's view that combination does not take place below certain limiting partial pressures of the gases is more profitable than Rayleigh's supposition. In these experiments the presence of water vapour did not appear to be essential. Gilchrist has shown that the conditions must be such that the phosphorus vapour can accumulate; thus, the intermittent effect is best observed when the phosphorus is at the bottom of a vertical tube.

Against the views of Jorissen and others based on the propagation of combustion in an explosive mixture, Iyer has raised objections on the grounds of his observations that the effect can take place in an open vessel in presence of some of Rayleigh's inhibitors such as naphthalene or carbon bisulphide, particularly if the vessel is wet with water. No effect was seen if water was used alone. The luminous pulses were observed to creep slowly along the surface of the vessel. The effect can be conveniently produced by soaking a piece of filter paper in a very dilute solution of phosphorus in carbon bisulphide and suspending it in an open glass vessel.

Thorpe and Tutton describe a fluctuating glow in a sealed tube containing phosphorous oxide and oxygen, and Scharff found that both phosphorous oxide and phosphorous sulphide exhibit periodic luminosity under a diminished pressure of oxygen. The pulsating glow of phosphorus trioxide has also been observed by Emeléus.

Other Periodic Reactions.—Other cases in the older literature of periodic phenomena which have not received confirmation at the hands of more recent investigators are the interaction of sodium sulphate and calcium carbonate studied by Malaguti and the report by Buff and Hoffmann that, in the decomposition of carbon dioxide by electric sparks, the carbon monoxide and oxygen recombine with explosion at a definite moment, the cycle being repeated indefinitely.

The observation has been made by Davis and Eyre that the rate of hydration of cellulosic fibres, gelatin and certain anhydrous salts takes place in a series of discontinuous steps. The change was followed by taking readings at short time-intervals of the gain in weight of the substance when left in air saturated with water vapour. Crowther and Coutts, using a continuous-reading balance, were not able to confirm these results in the case of the rehydration of anhydrous copper sulphate, and Fisher,

who could not repeat the observations with fabrics, has suggested that the discontinuities may be due to internal movements in the fabric.

An alleged periodic reaction is reported by Wedekind, but the present authors find considerable difficulty in regarding it as such. The residue obtained by heating zirconium earth with magnesium powder in a crucible was collected on a filter paper and washed with water. At a definite moment a small part of the substance came through with the washings in the form of a colloidal solution. Further washing gave a clear filtrate. By treating with dilute hydrochloric acid and then resuming the washing with water the appearance of the colloidal filtrate was repeated. By alternate washing with hydrochloric acid and water the phenomenon could be repeated indefinitely, but many substances would behave in the same way if they were subjected to such external periodic treatment.

Holker [1] has shown that when potassium oxalate is added to calcium chloride solution, the opacity of the precipitated calcium oxalate varies with time in a damped oscillatory manner. This seems to be due to some periodic change in the size of the particles.

Periodicity in Homogeneous Systems.—The foregoing examples are heterogeneous in nature, but cases have been reported of periodic reactions in homogeneous systems in addition to the example given by Bray (p. 57). Plotnikow,[1] made the observation that in an unknown light reaction between carbon tetrachloride and chlorine, the concentration of chlorine varied periodically with time. He [2] has also observed that although plants at constant temperature and under radiation with monochromatic light grow continuously, yet if light of two or more wave-lengths be used, the rate of growth is periodic. A periodic bleaching of dyes under the action of light is also mentioned.

A better-known example, described by Morgan, is the periodic evolution of carbon monoxide from the decomposition of formic acid by sulphuric acid. Between 40° C. and 70° C. this reaction goes in well-marked periods of gas evolution alternating with quiescent intervals. In presence of porous pot or other similar material the reaction proceeds steadily so that this phenomenon is generally understood to be a result of supersaturation of the liquid by carbon monoxide. On the other hand, the observation that very pure formic acid did not exhibit the phenomenon but that periodicity could be induced by adding small quantities of ethyl, methyl or amyl alcohols, gelatin and dextrin, does not seem consistent with a simple saturation hypothesis. The

authors are informed (private communication) that Morgan himself now considers the periodicity to be more deep-seated than this.

Periodic Enzyme Action.—In connection with periodic phenomena associated with colloids which have been described in a previous chapter, it is interesting to note that several reports have been made of periodicity in enzyme action. Among these is the observation of Groll [1] that the hydrolysis of urea by urease follows such a course.

In Groll's experiments, a solution of urea was buffered with potassium phosphate and kept in a thermostat at 35° C. after the addition of urease. The amount of urea hydrolysed was estimated by blowing the ammonia by means of a current of air into standard sulphuric acid and titrating. The activity of the ferment was found to vary periodically with time. Less marked periodicity was obtained at temperatures of 45°, 55°, and 65° C. and with rising temperature the rate of reaction approximated more and more closely to the curve for a monomolecular reaction. It is important also to note that old preparations appeared to lose the periodic property. De Bruyne, working with Groll, found the rate of formation of sugar from starch by the action of ptyalin to vary in a periodic way.

In order to test the view that these peculiar variations in rate were connected with the colloidal nature of the enzymes, Groll investigated the action of colloidal sols of platinum and gold. The method was to withdraw samples from stock at regular time intervals and measure the rate at which the sample decomposed a standard solution of hydrogen peroxide. The results were remarkably irregular, but the variations were so rapid as to preclude a detailed examination. Similar experiments on the variation in activity of platinum sols with age were carried out by Rocasolano,[1, 2] who also obtained indications of periodicity. Von Euler and Brandting conducted experiments at temperatures ranging from 17·5° to 50° C. and were unable to confirm the periodic activity of urease reported by Groll. The work was repeated successfully, however, by Wester and was later again confirmed by Groll himself.[2]

Went has described a periodic rate of production of diastase by cultures of *Aspergillus niger*. The wave-length was in this case some two or three weeks. E. Köhler finds that the processes of fermentation and of multiplication of yeast exhibit a certain periodicity. Sluiter determined daily the activity of a solution of lipase by shaking with an equal volume of milk for 24 hours at 39° C. and titrating the free acid with decinormal alkali. The activity was found to change irregularly in periods

of several days. Richet [1, 2] has reported irregularities in lactic fermentation in presence of certain antiseptics such as mercuric chloride. According to Lumière these observations are due to the use of inocula from non-uniform bacterial suspensions. If the latter are well shaken, uniform results are obtained.

In all these instances the periods are characterized by a certain irregularity which is to be observed in the curves obtained by Hedges and Myers [2] for the rate of decomposition of hydrogen peroxide by catalase.

An interesting example of biological periodicity, which may have its origin in this periodic ageing phenomenon, has recently been observed by Ehrenberg. Analysis of human brains and livers gave periodicity with respect to age for the total nitrogen and phosphorus content. Similar results were obtained with mice and rabbits.

Periodic Phenomena in the Adsorption of Gases.*— In 1922 Bangham and Burt carried out a series of experiments in which they measured the rate of adsorption of different gases by surfaces of glass. They obtained straight lines by plotting the logarithms of the quantities of gas taken up against the logarithms of the time of exposure to the gas. Close examination of the plotted results (especially those for low working pressures) revealed a curiously regular waviness,† which they attributed at first to optical distortion such as might occur whenever the rising mercury meniscus (by which the pressure was measured) passed behind one of the engraved lines of the glass scale. The waviness was still more apparent, however, in the experiments of Bangham and Sever, in which the optical method of measuring pressures was discarded.

Experiments by Bangham and Bloomer on the rate of oxidation of the metals in dry oxygen at low pressures have established, with a greater margin of certainty, the occurrence of periodic phenomena. The time-oxidation curves found by them for nickel, for example, consist of a series of steps, each of some minutes', or even hours', duration. The steps are less apparent under conditions favouring the rapid attack of the metal, and then appear as wavy irregularities superimposed on the general trend of the curves.

The effect was found to be greatly magnified in a case where the surface of the copper had been "cold-worked" by rubbing with emery powder, and was exposed to oxygen at a fairly

* Private communication from Mr. D. H. Bangham.

† This effect is almost imperceptible in the published graphs (*Proc. Roy. Soc.* 1924, A **105**, 481), but is apparent when the observations are plotted on a large-scale diagram.

low temperature without annealing. Under these conditions a thoroughly annealed piece of foil would have caused the absorption of only an insignificant quantity of oxygen during the first few hours (presumably owing to the scarcity of oxide nuclei), following which absorption would have taken place at an increasing rate, as the copper/copper oxide interface became more extended.* What was observed in the case of the cold-worked foil was that during the " induction " period the copper repeatedly took up small but significant quantities of gas, only to yield them up again immediately after; the foil continued this " breathing " more or less regularly every two or three minutes for several hours.

The important point in connection with this surprising result is that the direction of the chemical change was actually reversed at each half-period. As there is reason to believe that copper oxide nuclei, once formed, would continue to grow,† it seems necessary to assume that the periodic absorption was due to a reversible association of the gas with the metal—in fact, to adsorption.

It is interesting to note that in his experiments on the fatigue of the photoelectric effect with zinc, Allen observed small undulations superposed on the general trend of the time-curves. The variations had a period of about 10 minutes. In view of the well-known effect of absorbed gases on the " contact " E.M.F.s of the metals, and when it is remembered that this E.M.F. must be overcome by the electrons escaping from the metal, this result may possibly be taken as indicating that here, also, the action between the gas and metal was periodic in character. The periodicity was observed both with polished and with amalgamated zinc surfaces. It should be remarked that Allen, while admitting the possibility of periodic chemical action, ascribed the undulations to other causes.

Spasmodic effects of a much more marked character are recorded by Richardson from his experiments on the emission of positive ions (charged atoms of oxygen) from hot platinum wires in an atmosphere of oxygen. Under conditions sufficiently constant to maintain the current constant to within 5 per cent. under normal conditions, Richardson observed at successive 2-minute intervals the following relative values for the positive current in oxygen: 146, 180, 178, 228, 158, 170, 150, 246, 166, 324, 198, 174, 198. After discussing his attempts to track down the cause of this uncontrolled variation, Richardson

* Pease and Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179; Taylor and Jones, *J. Phys. Chem.*, 1923, **27**, 623.

† Cf. Pease and Taylor, *loc. cit.*

states : " There seems to be no escape from the conclusion that this effect is caused by some periodic change in the state of the platinum surface. If the metal was continually undergoing recrystallization accompanied by the emission of absorbed gas, equilibrium might possibly be incapable of ever being attained, and the results might simulate those observed." The effect was more marked at high than at low pressures. It is important to note that since under identical conditions the negative (electron) emission was quite steady, variations of the " contact " E.M.F. cannot have been either caused by, or resulted from, these fluctuations.

CHAPTER VII

PERIODIC ELECTRO-CHEMICAL PHENOMENA

It is convenient to consider the work on this type of periodic reaction in two sections :

(*a*) Cases in which current is taken from the system.

(*b*) Cases in which current is led into the system : and this section may be further subdivided according to whether the phenomenon occurs at the anode or at the cathode.

The earliest case of periodicity of the first type was reported in 1828 by Fechner, who observed fluctuation in the potential of an iron electrode immersed in a weakly acid solution of silver nitrate and a corresponding periodic deposition and dissolution of silver. Similar observations were made a few years later by Schönbein,[1] using iron in contact with copper. Kistiakowsky[3] obtained a periodic current from the cell—Fe (rusted)/5 per cent. $K_2Cr_2O_7$,*N*-H_2SO_4 /Fe (periodic)—in which the electrode responsible for the periodicity consisted of the purest iron, scrupulously cleaned and polished and immersed in 10 per cent. sulphuric acid before the experiment. By employing two electrodes of similarly treated iron in the same solution he [1] succeeded in constructing a cell which produced an alternating current, the two electrodes periodically reversing in polarity. It is interesting to observe that in this instance the metal received a quite definite form of treatment and that the treatment is such as to produce what we have called an activated surface.

Kistiakowsky [2] also observed an alternating passivity and activity of iron in dilute nitric acid, chromic acid or potassium permanganate solutions.

Brauer extended Ostwald's observations (Chapter IV) on the periodic dissolution of a particular non-reproducible batch of chromium in hydrochloric acid, making a special study of the electrochemical relations. Constructing a cell of ordinary and periodic chromium electrodes immersed in dilute hydrochloric acid, he showed that the periodic chromium was in the " inert " state cathodic and in the " active " state anodic to ordinary chromium. The total difference in potential was of the order of 0·1 volt and it was concluded that the alternation was not, as Ostwald had supposed, between the chemically active and passive states since the chromium remained chemically active

throughout. In the majority of Brauer's experiments the chromium was fixed to a platinum support which was itself lowered into the solution. This seems an unfortunate method of experimentation, for the observed potential difference depends in such a case on the relative amounts of chromium and platinum immersed. Experiments with one piece of chromium and different platinum supports gave very different results, the reaction being in some cases not periodic at all. These discrepant observations receive, however, a reasonable explanation by the experiments described in Chapter IV on the use of platinum as an activating agent for metallic systems.

Brauer confirmed Ostwald's observation that other specimens of chromium did not exhibit periodic properties, but found that minute waves were sometimes induced by the addition of arsenious oxide. In this case, it would appear that by reduction an active second metallic component was introduced into the system.

Bredig and Weinmayr found the potential difference between mercury and hydrogen peroxide to vary periodically, synchronizing with the periodic evolution of gas, and these experiments were repeated in greater detail by Antropoff.[1]

Heyrowský mentions sudden changes and fluctuations between the values 0·77 and 1·67 volts for the E.M.F. of the cell Hg/Hg_2Cl_2,*N*-KCl/Al, and this observation may be regarded as similar to the periodic dissolution of aluminium amalgam in hydrochloric acid described by Hedges and Myers.

Periodic Phenomena accompanying Electrolysis

Anodic Periodicity.—Schönbein [2] led a current through the cell $\overset{+}{Fe}/dil.H_2SO_4/\overset{-}{Pt}$ and observed that the current soon dropped to a very small value due to "passivation" of the iron, but, by short-circuiting the electrodes through a suitable resistance, the current passing through the cell became periodic, the iron behaving as though it were alternatively active and passive.

About the same time (1844) Joule became interested in the irregular movements of a galvanometer needle, which he had repeatedly observed in the electrolysis of sulphuric acid with iron electrodes, and carried out more careful experiments both with iron and zinc electrodes. Using an amalgamated zinc rod as anode and electrolysing dilute sulphuric acid with 6–10 Daniell cells, a pulsating current always started after a time. A visible change accompanied the periodic variation in current density. Joule writes: "It was natural enough to suppose that such extraordinary irregularities might be accompanied by a visible

change in the character of the electrode, and in this I was not deceived, for on examining the amalgamated zinc I observed the following very curious phenomenon :—At intervals of one or two seconds a white shade overspread the surface of the amalgamated zinc and then suddenly disappeared, leaving the metal brilliant. The pulsations of the current were evidently simultaneous with these sudden changes in the appearance of the electrode and the needle received a sudden impulse every time the white film suddenly broke away." Passing the current from three Daniell cells through dilute sulphuric acid, using an amalgamated zinc cathode and an anode of iron wire, Joule noticed alternate periods of dissolution of iron and evolution of oxygen, each state lasting about half a minute. In discussing the phenomenon, Joule makes the following most important observation : "A great deal depends on the quality of the iron employed. With some specimens of iron and steel, I could not succeed at all, whilst with a piece of rectangular iron wire a quarter of an inch broad and one-eighth of an inch thick, I was able to obtain intermittent effects when using a battery consisting of two, three, four and even five cells of Daniell."

Heathcote states that when a current was passed through the cell $\overset{-}{Pt}/HNO_3,(d)1{\cdot}4/\overset{+}{Fe}$, the needle of an ammeter placed in series exhibited oscillations of a regular kind. Different results were obtained from different samples of iron, and it may be mentioned that in most of these cases the influence of minute traces of impurities is not excluded and the phenomena are quite probably due to a cause similar to that operating in Ostwald's case. On the other hand, there may have been an "autoperiodicity" (see p. 78) in certain of the specimens.

Fredenhagen [1] electrolysed sulphuric acid with an iron anode and obtained a periodic current after addition of chlorine ions. Bromine and iodine ions were also active in bringing about periodicity.

The periodic dissolution of iron in sulphuric acid due to anodic polarization was studied in greater detail by Adler. In these experiments the concentration of the acid was without influence, the most important factor being the current density, The frequency decreased with increasing current density and increased with rise in temperature up to 30° C., after which the current became constant. Addition of colloids was without influence. Adler showed that the periods were not, as has so often been supposed, due to the periodic breaking of an oxide film, since it was observed that specimens of iron remained periodic in presence of potassium permanganate when permanently enveloped in such a film. In place of iron, experi-

ments were conducted with electrodes of pure chromium, nickel and copper, but periods were not observed. These gave periods, however, when alloyed with iron.

Smits [1, 2, 3] found that with certain current densities an iron electrode immersed in a solution containing a mixture of ferrous sulphate and ferrous chloride gave a potential rapidly alternating from a positive to a negative value with an amplitude of 1·74 volts. This is explained as being due to the periodic acceleration of establishment of inner equilibrium in the metal by chlorine ions, but it is admitted that such an explanation cannot explain Adler's results.

Periodic electrolytic phenomena occurring at the anode have been reported in respect of metals other than iron. Müller observed pulsations in the potential of a manganese anode dissolving at current densities between 0·075 and 0·15 amp. per sq. cm. in weakly acid sodium phosphate solution. Hydrogen was evolved at the lower values of potential and a mixture of hydrogen and oxygen came off at the higher values. Byers observed a similar effect using a cobalt anode dissolving in sodium sulphate solution or in sulphuric acid at very high current densities. Periods of oxygen evolution, during which the metal remained lustrous, alternated with periods of dissolution of cobalt, during which the anode became dull.

Liebreich describes periodic phenomena in the electrolysis of chromic acid, and according to Kleffner the phenomenon only occurs when the solution contains free sulphuric acid. Kohlrausch reported that when electrolysing platinum tetrachloride for the purpose of preparing pure platinum, he had once obtained a periodic evolution of gas, but subsequent attempts to repeat this had proved unsuccessful.

Periodic changes in anodic potential and current density were observed by Köhlichen and by Küster [1, 2] during the electrolysis of solutions of alkali sulphides using platinum electrodes. The seat of the periodicity was shown to be at the anode, which became covered periodically with a film of sulphur. This periodicity was evident only between certain limiting current densities, and these limits depended on the concentration of the solution, its sulphur content and temperature. A certain amount of polysulphide was necessary and to ensure periodicity it was best to use sodium sulphide, to which flowers of sulphur had been added, and to employ a current density of 10–20 amps. per sq. dm. The general conclusion was that the sulphur forms an insulating film over the surface of the anode, and reduces the current density so that electrolysis proceeds very slowly. In the meantime, the sulphur film slowly dissolves off the anode, forming

a polysulphide again. The current density then rises so that sulphur can be deposited afresh. Such a view of the case would, however, appear to lead to an equilibrium condition without any periodicity, and it fails in any case to account for the remarkable influence of the condition of the platinum electrodes. Manifold forms of waves are produced, varying from simple forms to complex figures showing secondary and tertiary waves. The most important factors in the formation of waves was found to be the size, position and *surface nature* of the platinum electrodes. With many specimens of platinum, no periods at all were obtained. A rough platinum surface appeared to be most satisfactory, and one can hardly escape the conclusion that periods were only obtained when the platinum was in what we have called the active condition.

Another possibility which must not be overlooked is that in many of these examples the product may be deposited in a metastable condition at the high current density employed and may of itself give rise to periodic phenomena. This seems to be the case in some reactions involving the deposition of metals described later in the present chapter. Experiments on electrolysis (Hedges) seem to indicate that non-metallic deposits can also act in this way.

Kremann and Schoulz observed precisely similar phenomena in the electrolysis of alkaline iodides, and in this case the tendency to periodicity was observed to be parallel with the tendency to form polyiodides, i.e. in the order Cs, Rb, NH_4, K, Li, Na. Some very irregular waves, typical of those obtained when the activating agent is a metal, are given.

Experiments on the periodic electrolysis of ammoniacal nickel salt solutions between platinum electrodes were conducted by Windelschmidt and by Dietrich. The latter recommends a solution containing 5 grams nickel ammonium sulphate and 25 c.c. concentrated ammonia, made up to 150 c.c., the electrolysis being carried out at 45° C. In such ammoniacal solutions a film of nickel hydroxide forms periodically over the anode surface, and simultaneously the anodic potential rises and the current density falls off. The periods commence when only about 3 or 4 per cent. of the original nickel is left in solution, and continue till all is deposited. Rotation of the anode increased the frequency, and the amplitude increased with increasing current density. Experiments were also carried out in presence of ammonium oxalate, using a solution prepared by making up 1 gram crystallized nickel sulphate and 6 grams ammonium oxalate to 150 c.c. with water and electrolysing at 75° C. with a current density of 0·7 amps. per sq. cm. Using potassium oxalate

or replacing the nickel sulphate by nickel chloride, periods were not obtained, but cobalt sulphate could be used successfully.

More recently, oscillating anodic potentials have been observed by Robertson in electrolysing a solution of potassium ethyl malonate with gold electrodes.

Cathodic Periodicity.—Förster found the deposition of copper from a strongly acid solution to be periodic at high current densities, and a similar case is quoted by Cohen in electrolysing an acid solution of bismuth nitrate. Kremann and Suchy observed a periodically changing cathode potential in the deposition of a 50 per cent. iron-nickel alloy from a solution containing 0·45 *M* ferric sulphate and 0·6 *M* nickel sulphate. The current oscillated between 0·3 amp. and almost zero. It is suggested that the explanation is to be sought in local currents in the alloy.

Coehn electrolysed a solution of an alkali salt with a mercury cathode and noticed that the surface of the mercury alternately became grey and bright, and hydrogen was evolved during the bright periods. The course of the phenomenon was registered photographically by Kremann and Lorbeer. It may be mentioned that it is the view of the present authors that mercury is the one metal which is normally periodically active.

Haber mentions the observation of periods in the electrolytic reduction of nitrobenzene in alcoholic solution at a platinum cathode. Mention must also be made of the pulsations of a mercury surface in a capillary electrometer described by Roshdestwensky and Lewis. This phenomenon occurred when using mercuric cyanide in the electrometer and was limited by certain ranges of potential difference. When a potential difference rather more than one volt was applied, making the mercury the cathode, a period of induction lasting about 6 minutes, during which the mercury thread rose steadily up the capillary, was succeeded by a series of oscillations with time intervals of 6–38 seconds. The amplitude was observed to increase with rising E.M.F.

MacInnes and Adler record periodic fluctuations at very low current densities in the hydrogen overvoltage of a zinc electrode in sulphuric acid. Each period, however, corresponded with the rise of one bubble of hydrogen, so this cannot be considered to be true electrochemical periodicity.

Electrochemical Investigation of the Periodic Dissolution of Metals.—So many of the observations described in the previous pages are explicable in terms of the phenomena associated with "activated" metals, described in Chapter IV, that it seemed desirable to the present authors [4] to investigate

those causes of periodic metal-dissolution, where a considerable amount of data is already to hand, from the electrochemical standpoint. This method not only furnishes a delicate means of following the course of reactions where the rate of gas evolution is so slow as to render the manometric method inapplicable, but also provides data which are of importance in elucidating the mechanism involved in the periodic dissolution of metals. Further, the method has considerably wider scope, being well adapted in particular to the case of reactions involving the deposition of metals.

In this work the measurements of potential were made by means of a Dolezalek quadrant electrometer, the needle of which was charged to 90 volts by means of a battery of dry cells. The system consisted of one or more metal electrodes immersed in the appropriate solution contained in a glass bottle of 100 c.c. capacity, which was fitted with a wide rubber stopper carrying glass tubes, through which the electrodes were sealed. The reading scale was so placed that one volt gave a deflection of 273 scale divisions (mm.). By means of a bridge of saturated potassium chloride solution leading to an auxiliary saturated calomel electrode, it was possible to determine the potential difference between either the two metal electrodes immersed in the solution or between each metal and the standard reference electrode. In either case, one electrode was earthed and the other connected to one pair of quadrants of the electrometer, the other pair being earthed also. The metals were suspended by fastening to a stout platinum rod by means of a platinum screw. The rod was soldered to copper wire and this was sealed into glass by wax. For the purpose of comparing the chemical and electrical effects in some of the systems, the apparatus was combined with that described in Chapter IV, so that the course of the reaction could be followed simultaneously on the electrometer scale and on the manometer.

The two sets of curves agree very closely when the frequency and amplitude of the periods are not great, but in order to register the short waves electrically, it would be necessary to use a dead-beat instrument. The natural period of the electrometer needle as suspended in these experiments was 16 seconds. Simultaneously readings of potential and gas pressure were taken every 30 seconds, and the potentials recorded are expressed with reference to the saturated calomel electrode. All experiments were carried out at room temperature.

Examination of some Metal Systems.—It has been already shown that certain metallic couples dissolve in acids in a periodic manner after the second metallic component (i.e. the cathodic

metal which does not dissolve) has been treated or activated by certain processes. Graph 12 (Fig. 14) represents the potential against the saturated calomel electrode acquired by such a couple of magnesium and nickel sheet dissolving in 0·3 *N* hydrochloric acid, and below is plotted the synchronous variation in gas pressure. The periods are not very regular, but this is often a feature

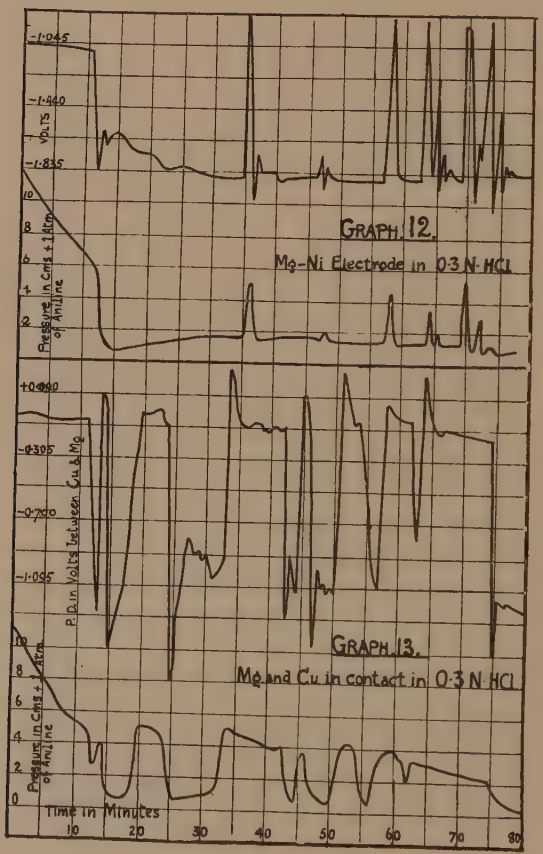

Fig. 14.

of systems where the activating agent is such a second metallic component. Simultaneous periodic curves of this type have been obtained with couples of magnesium with platinum, gold, cobalt and copper in ammonium chloride solution, and with aluminium in hydrochloric acid. In the example illustrated in the graph and in many of the other instances mentioned, the periodic nature of the gas evolution was easily visible to the eye.

It appeared that during the periods of high gas pressure the excess of hydrogen came from the nickel or other cathodic metal, the dissolving magnesium preserving at all times a slow and apparently steady rate of gas evolution. This is in accord with other experiments which indicate that the seat of the periodicity is the second metallic component.

In Graph 13 (Fig. 14) is recorded the periodic potential difference existing between electrodes of magnesium and activated copper in contact immersed in 0·03 *N* hydrochloric acid. Comparison of this with the foregoing graph shows that the periodic evolution of hydrogen is attended by simultaneous variations in (*a*) the potential of the couple as a whole with respect to the solution, and (*b*) the potential difference between the two components. In the latter case, the copper appeared to be quite inert so long as the high potential difference lasted, and when the potentials of the two metals approached each other, hydrogen was evolved from the surface of the copper.

Periods have not been obtained in experiments with platinum, gold, silver and nickel as activating agents when the cathodic and dissolving metals were not in contact.

Reactions involving the Deposition of Metals.—When magnesium is allowed to dissolve in dilute hydrochloric acid containing ferrous sulphate in solution, reduction takes place and iron is deposited as a black film on the surface of the magnesium. By suitably arranging the concentrations of the reagents, periodic phenomena may be observed in this reaction. This particular case was first found owing to the visible periodic changes which occur, and the system serves admirably as an optical demonstration of chemical periodicity. After an initial lapse of time dependent on the relative concentrations of the reagents, a film of reduced metal spreads from one or two centres on the magnesium surface until it covers about half the metal. Then it dissolves, leaving the electrode with a bright surface. Then the black film grows again, covering a greater surface of electrode, and afterwards redissolves, leaving a few black patches. These two processes alternate a number of times, and in each successive period both the area covered by the growing film and the area of the film remaining after the partial dissolution increase. This continues until finally the film, even in its partly dissolved state, entirely covers the electrode. There is no reason to suppose that the periodicity is then at an end, and it is probable that the film continues to grow periodically in thickness, since it can do so no longer in extent. When the surface is once complete no further change in potential is to be expected.

The change has been followed in the apparatus described,

making simultaneous observations of the potential of the dissolving metal, the pressure of the evolved hydrogen and the appearance of the film. The electrical change was found to synchronize exactly with the chemical change indicated by the appearance of the film. The potential of the magnesium became more positive as its surface was covered by the growing film of iron and returned in the negative direction as the surface brightened with the dissolution of the film. The mean amplitude of this change was generally about 0·03 volt, and the amplitude was observed to decrease throughout the experiment, consistently with the relative areas covered by the film at the maxima and minima of successive waves. The hydrogen evolution was steady throughout.

The frequency of the periods was found to increase with the concentration of ferrous sulphate, and to be independent (between the limits of 0·6 *N* and 0·2 *N*) of the concentration of acid. In general, the frequency of other periodic reactions is proportional to the concentration of the reagent and decreases with increasing amount of activating agent. The hydrochloric acid and ferrous sulphate are not to be regarded, therefore, as reagent and activating agent respectively, but rather the ferrous sulphate is the reagent and the reduced iron an active second component. This view is also consistent with the absence of periodicity in the rate of hydrogen evolution. Experiments have been carried out in which the solution was vigorously stirred by air without any interference with the phenomena described, so that the possibility of a periodic diffusion of reactants or reaction products is ruled out.

Graph 15 (Fig. 15) represents some of the experiments which have been carried out on this system, and shows the effect of varying the concentration of ferrous sulphate between the limits 0·01 per cent. and 0·05 per cent. of $FeSO_4.7H_2O$, the hydrochloric acid being kept at 0·3 *N* strength. In an experiment in 0·3 *N* hydrochloric acid with the addition of 0·1 per cent. crystallized ferrous sulphate, the periodic film formation was observed during the first three minutes, after which the permanent deposit set in so that electrical measurements could not be taken. It is probable that in stronger solutions, where the deposition takes place immediately after immersion, very rapid periods, incapable at present of detection, are actually existent.

When hydrochloric acid was replaced by 0·3 *N* sulphuric acid, no periodicity was observed, the reduced iron gradually forming a permanent deposit. Experiments have also been conducted in hydrochloric acid in which ferrous sulphate has been replaced by an equivalent quantity of nickel chloride or cobalt chloride.

In the former case, reduction did not take place in acid solution, and in neutral solution the hydroxide was formed. Reduction of cobalt chloride took place in both hydrochloric and sulphuric acids, but a permanent deposit formed without the advent of periodicity. In ammonium chloride solution the phenomenon was more marked than in hydrochloric acid, but this system does not serve well from a quantitative point of view, since the solution becomes alkaline with ammonia and reacts with the metallic salt. Periodic phenomena similar to those already described have been observed with magnesium dissolving in

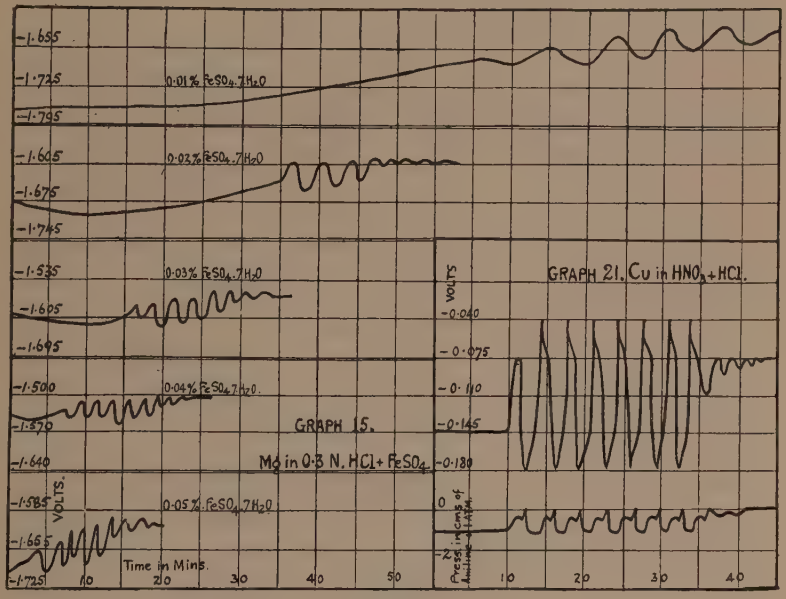

FIG. 15.

2 per cent. ammonium chloride solution, with addition of 0·001 per cent. crystallized cobalt chloride, 0·05 per cent. crystallized ferrous sulphate, 0·001 per cent. crystallized nickel chloride, or 0·002 per cent. crystallized copper sulphate. The smallness of the quantities involved is a further example of this characteristic feature of periodic chemical action.

In all these instances the rate of hydrogen evolution was also periodic. This may be a secondary effect, for it has been shown* that couples of magnesium with these metals reduced in ammonium chloride solution are very active, decomposing water at the ordinary temperature. It is to be expected, therefore,

* Hedges and Myers, *J. Chem. Soc.*, 1925, **127**, 495.

that the rate of evolution of hydrogen would under these conditions be dependent on the area of magnesium covered by the reduced metal.

"Autoperiodic" Systems.—With a view to obtaining periodic phenomena from the simplest reacting systems, continuous measurements of the electropotential of single activated metals reacting with a suitable solution were made. The object was to dispense with a separate second metallic component and to incorporate it with the dissolving metal so that the reacting electrode might function as its own activating agent.

Some experiments were carried out with aluminium, magnesium and zinc, after treatment by the usual methods. The positive results obtained in these experiments served to demonstrate the possibility of constructing "autoperiodic" systems, though these particular cases did not lend themselves to quantitative development. The feeble activation which could be induced in these metals was very probably on account of the difficulty of hardening them, and for this reason subsequent attention was devoted to copper, which has been found to be easily susceptible of activation. In all the experiments cited below, the copper was activated by cold-rolling to the specified thickness from an original thickness of 0·022 inch.

Graph 21 (Fig. 15) was obtained from copper rolled out to 0·0105 inch, dissolving in an acid mixture containing 25 c.c. nitric acid of (*d*) 1·42, 10 c.c. hydrochloric acid (*d*) 1·16, and 65 c.c. water. The graph illustrates the synchronous periodic variation in the potential of the copper electrode, and in the pressure of the evolved gas. The gas evolved consists mainly of nitric oxide, which reacts with atmospheric oxygen with decrease in volume of the total gas. The fine capillary delays the entry of air, and the pressure of gas in the apparatus is therefore slightly below atmospheric.

The series of changes to be observed at the surface of the dissolving metal under these conditions is most striking. Initially, the surface preserves its natural colour; then there is a sudden appearance of a black film deposited in the form of vertical streaks; the black film next turns grey; this is followed by a sudden flash as the film turns white, and finally the film dissolves, leaving the metal with its original colour. Then the black film forms again, and the whole cycle of changes is repeated again and again. After the point where the amplitude of the waves suddenly decreases (see Graph 21), the alternation is between the black and grey films and the white film no longer appears. Finally, a permanent black film sets in, and the pulsations cease.

The onset of the black film is marked by a movement of the electropotential in the positive direction, and by an increase in the rate of evolution of the gas, whilst, corresponding with the gradual turning grey of the film, the electropotential and gas pressure slowly move towards their former values. The sudden appearance of the white film is accompanied by a rapid change of the electropotential in the negative direction, and an equally rapid increase in the rate of gas production. This latter effect is easily visible, and resembles a miniature eruption. As the white film dissolves, both the electropotential and the gas pressure regain their initial values.

The limits between which the concentration of the various components of the solution can be varied are narrow. Thus, the mixture 25 c.c. nitric acid, 10 c.c. hydrochloric acid, 65 c.c. water, always produced the periodic phenomena when acted upon by cold-rolled copper, but, keeping the total volume of solution at 100 c.c., and the hydrochloric acid constant at 10 c.c., mixtures containing 30, 27·5 and 20 c.c. nitric acid did not favour periodicity. Similarly, keeping the amount of nitric acid constant at 25 c.c. and the total volume at 100 c.c., mixtures made up with 15, 12·5 and 5 c.c. hydrochloric acid did not give a periodic reaction. Other more widely divergent mixtures were tried, but the reaction pursued a steady course. The best effect was observed using the ratio 25 c.c. nitric acid, 10 c.c. hydrochloric acid, and 70 c.c. water, making a total volume of 105 c.c. No periodicity was observed using either 45 c.c. or 55 c.c. water, whilst with 75 c.c. the electropotential and gas evolution were both periodic, but the film forming over the copper surface alternated between the grey and white forms and the black film never appeared. Further, the frequency was higher than in the other cases. Thus, under different conditions, the alternation may be between the grey and white, grey and black, or white and black films ; in the two former cases the amplitude of the electrical effect is correspondingly smaller.

Periodic Electrical Discharge.—Reports of intermittent discharges from points and in metallic arcs have been made, but these are almost certainly different in kind from the periodicity which has been referred to in the preceding pages. Examples of such discharges are quoted by Cady, who states that the current employed should be small, and the external circuit capacity large. The Cooper-Hewitt mercury interrupter is cited as an example of an intermittent arc. Crowther and Stephenson have studied the Wehnelt electrolytic interrupter from this point of view.

Bär, Laue and Meyer describe oscillations in the helium arc

at voltages below the first radiating potential, and these observations have been confirmed by Eckart and Compton, [1, 2] who also found such oscillations in mercury-vapour arcs, but did not observe them using diatomic gases. The earliest mention of such oscillations seems to have been made by Kannenstine. Recently, additional examples have been described by Kwei.

CHAPTER VIII

PERIODICITY AND THE METASTABLE STATE

Although it is not possible at present to formulate a thesis which can give a complete explanation of the various manifestations of periodicity, the authors' experiments with metals have led to the recognition of certain conditions which appear to be essential in all the cases so far investigated. There is a certain amount of evidence to suggest that such conditions are operative not only in other types of periodic reaction, but also in periodic structures and in cases of static periodicity. To this extent it is possible to consider the whole domain of physico-chemical periodicity from one aspect and to put forward the suggestion that periodicity is a characteristic property of a certain metastable state of matter.

The experiments described in Chapter IV demonstrate that in these cases periodicity is only realized in the presence of a third constituent, that this additional agent may be a second metallic component, and that the source of the periodicity is in this activating material. The activating material may be in the form of a metastable condition of the reacting substance or it may be a metastable form of a non-reacting constituent. It follows that the phenomenon may be traced to some change which takes place in the second metallic component in consequence of the treatment it receives. The authors are of opinion that the periodicity in these instances is associated with a metastable, close-grained and possibly amorphous form of the metal, and the evidence on which this view rests will now be given.

Reviewing the various methods of activation which have been employed, the most effective is mechanical deformation by heavily scraping the surface, or better by cold-rolling. The question as to the exact nature of the change taking place in metals as a result of cold-work appears to be still in dispute, but the vast amount of literature which has been published leads to the conclusion that crystal-grain size is of fundamental importance. Whether a certain amount of amorphous metal is produced by distortion of the space-lattice, or whether films of amorphous metal bounding the grains are increased in extent, it is very plain that a real change takes place. The metal increases in hardness and often becomes brittle ; the internal energy of the metal also is increased,

and the present authors [4] have found that a well-marked difference of potential exists between the active and inactive forms of a metal immersed in an electrolyte.

In fact, the process of activation appears to run parallel with the process of hardening. Very soft metals like lead and tin, which are known to anneal themselves spontaneously at the ordinary temperature after cold-working, have never yet yielded to any of the methods of activation, although particularly drastic means have been employed. This may be contrasted with the behaviour of hard metals such as nickel and cobalt. These metals appear to be normally active when in the form of sheet, because they retain for a long time the activity imparted to them through the rolling. Similar observations have been made by Schmidt,* who finds that the electropotential of most metals is lowered by rubbing with emery paper and traces a parallelism between the time taken to revert to the normal value and the hardness of the metal.

This reversion to the normal state is a recognized feature of the activated metal. When the distortion has been slight, as in vacuum-heat treatment, the metal loses its activity in a day or so, reverting to its normal electropotential value and refusing to induce periodicity in the systems. On the other hand, if the distortion has been great (e.g. after cold-rolling) the metal may remain active over quite long intervals. A sample of 0·022 inch copper sheet, which had been rolled out to 0·0085 inch, retained its inherent periodicity unabated after 42 days.

The great advantage of rolling over other forms of cold-work is that a more or less uniform treatment is given. In scraping or polishing, different parts of the metal surface are affected to different extents, and the result is a very irregular series of waves. It was in an attempt to secure a uniform condition of activity over the surface that experiments were carried out using electro-deposited metals. Surfaces of electro-deposited copper were found to serve excellently as second metallic components, and it appeared that deposition at high current densities is desirable, since the resulting waves have a high amplitude. It is known that this is just the condition favouring a hard metal deposit and that the size of the crystal grains becomes smaller with increasing current density.† Similar conditions appear to apply to chemically deposited metals.

In the method of vacuum-heat treatment, all the metals were observed to give off varying quantities of gas, and this effect is

* *Z. Physikal. Chem.*, 1923, **106**, 105.

† Compare Blum, *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 213 ; 1923, **44**, 397.

very noticeable during cathode-ray bombardment. It appears that the change is consequent upon the liberation of gas from the surface layers, for it has been noticed that with any one piece of metal it becomes increasingly difficult to bring about activation by this method. With platinum, easy susceptibility to activation can be restored by coating the surface with platinum black. It thus appears that activation depends on the expulsion of gas from the surface molecular layers of the metal. When this has been done, fresh gas is adsorbed only on the outer surface and it becomes increasingly difficult to get gas from the inner layers. Platinizing the platinum gives a new start to the process. According to Beilby * " . . . a metal may be locally liquefied by the passage through it of minute bubbles of gas at temperatures many hundred degrees below its melting-point " and " . . . the gas molecules, as they find their way among the metal molecules of the solid, are quite capable of producing sufficient movement to arrest crystallization, or even to flow the crystals which are already formed into the amorphous, vitreous variety." Finally mercury, which can be regarded as the ideal amorphous metal, is the one metal which is found to require no process of activation. On the other hand it does not lend itself very easily to employment in chemical reactions.

It may not be out of place to recall attention to what have been described in Chapter II as the static periodic properties of metals. It is difficult to visualize a direct connection between these observations and the work on periodic chemical reactions, but it is significant that these static periodic properties are associated with a state of the metal similar to that which gives rise to the time-periodicities, and it may be that both types of phenomena are the results of the behaviour of a metastable state of the metal towards different forces and conditions.

There is no reason to suppose that these properties are peculiar to metals only: indeed, there is evidence to the contrary. Metals have been examined chiefly for reasons of experimental convenience, and in particular on account of their adaptability to electrical methods of measurement. There is every reason to believe that periodic properties may be associated with the metastable, amorphous forms of substances other than metals. Colloids immediately suggest themselves and, as the preceding pages show, the cases of periodicity connected with colloid systems are numerous. There is a very close analogy between a close-grained metal and a colloid system.

The examples of periodic chemical reactions which have been discussed are characterized in the main by heterogeneity of

* *Aggregation and Flow of Solids*, Macmillan, 1921, pp. 45, 175.

conditions : that is to say, the reactions take place at surfaces, and for periodic action it is believed that these surfaces must be in the condition which has been described. Examples have been quoted, however, of periodicity in homogeneous systems, but it is to be observed that in these instances the exact nature of the reaction is obscure.

Considering the periodic luminosity of phosphorus, there has been considerable discussion as to whether the effect is a concomitant of a direct oxidation of phosphorus to the pentoxide, or whether, since the trioxide itself glows during oxidation, the reaction takes place in two stages, light being emitted during the oxidation of the intermediate phosphorous oxide to the final product. Although the question appears to be still open, there is some evidence to support the second view.* In that case, since the reaction takes place in the vapour phase, the periodicity may be traced to the colloidal particles of phosphorous trioxide, which undergo further oxidation by a periodic process. It is interesting that Rayleigh's view of the matter requires the presence of nuclei, so introducing heterogeneity into the system.

The decomposition of hydrogen peroxide by iodine in homogenous solution reported by Bray may nevertheless be controlled by surface properties. Apart from the possibility of colloidal iodine, this is the type of reaction where the surface of the containing vessel is an important factor and sometimes the sole seat of reaction. The authors have often had suspicions that glass surfaces do sometimes act in a periodic way in virtue of their metastable, amorphous structure. Holker has also experienced interference by the surfaces of vessels. On the other hand, Bray's case may be an instance of mathematical periodicity after the style of Lotka's equations due to the collusion of a series of simultaneous or consecutive reactions.

In the case of Holker's phenomenon and also in rhythmic structures, the process only becomes periodic when the product is in such a state as to expose a large surface and one which in its freshly formed condition is very likely to be in the state which has come to be recognized as active. This throws up the ageing effect in a new light : old colloid preparations do not give periodic results because the surface has reverted to the inactive, stable form.

There are thus considerable grounds for the view that periodicity in chemical reactions is associated with surfaces which are in a metastable condition, and it now becomes of interest to consider the extent to which surface tension plays a part in the

* For spectroscopic evidence of this and a review of the position, see Emeléus, *J. Chem. Soc.*, 1925, **127**, 1362.

phenomenon. It is a significant fact that periodic surface-tension phenomena are not unknown. Mention is made by Quincke[1,2] of the periodic spreading and accumulation of oil drops on a large water-air surface such as a pond. These pulsations were found not to go on a surface of pure water, so again the conditions are very delicate.

More elaborate experiments were conducted by Quincke [2,3,4] on pulsating surfaces. A bubble of air in water is trapped under a plane glass surface and kept under observation : on addition of alcohol the bubble contracts because of the alteration in surface tension. If the alcohol is added to the water in the vicinity of the bubble extremely slowly from a fine capillary (so slowly that 1 c.c. is added in several hours) the bubble is observed to pulsate, contracting and expanding rhythmically in periods of 0·1 to 10 seconds according to the speed of addition of alcohol. Precisely similar pulsations were observed in the case of an oil drop in water when sodium carbonate solution was allowed to flow very slowly from a capillary 0·1 mm. in diameter in the neighbourhood of the drop. The oil contained fatty acids with which the sodium carbonate could form a soap. The wave-length or time interval between the pulsations was observed to increase throughout an experiment. An analogous case was observed earlier by Paalzow, who noticed pulsations in a mercury drop placed near a crystal of potassium dichromate, both being immersed in dilute sulphuric acid so that the dichromate could slowly diffuse towards the mercury. Wiedemann made the observation that when a drop of mercury in dilute sulphuric acid is made the anode of an electrolytic cell it spreads out and becomes covered with a film : the film then breaks and the drop regains its spherical form and these two states continue to alternate in regular periods. In this connection reference may again be made to the observations of Roshdestwensky and Lewis (*q.v.*). Weber reports that when aqueous gamboge is allowed to spread into a film of alcohol containing air bubbles held between two glass plates, a pulsating circulation in periods of about one second may be observed to occur round the bubbles.

When experiments are carried out under these conditions the air bubble or drop of oil or mercury is subject to a progressively increasing concentration of alcohol or other substance and the result is a periodically changing surface tension. It may be that, at all " active " surfaces, surface tension becomes a periodic function of concentration. The work on periodic chemical reactions is easily explained on such a hypothesis, for lowering of surface tension facilitates chemical interaction. Holker's phenomenon also becomes quite clear, for if the amount of energy

involved in the formation of the precipitate-liquid boundary is large, then the precipitate will consist of a relatively small number of large particles for the sake of economy in energy. If, on the other hand, this amount of energy is small, the precipitate will be able to disport itself with a large surface and a large number of small particles will be formed. Periodic changes in particle size are therefore to be expected with progressive increase in concentration of the liquid, provided that the precipitate has the surface which has been described as "active." Actually Holker has found that the phenomenon can only be observed when the precipitate is of colloidal dimensions. Similar remarks apply to periodic structures such as Liesegang's rings. Recent experiments by Johlin indicate that the surface tension of a 0·1 per cent. albumen solution containing N/700 NaOH decreases periodically with time. In some preliminary experiments similar observations were made with solutions of salicic acid and other colloids.

Periodicity as a feature of the processes and functions of living organisms is so apparent that enumeration of examples seems unnecessary, but consideration of the heart-beat indicates that it is a feature of fundamental importance. It is not impossible that the same property is at work in these cases, for living organisms are made for the most part of colloidal matter. It may be that a periodic stimulus is caused by a progressive increase in concentration of some substance at an active surface in the organism. This is a matter for the future : for the present it is sufficient to show that periodicity is a feature of purely physical as well as biological systems.

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